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Total Suspended Particulates: Review & Analysis

Radian Corporation

Prepared For
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April 1976

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16. ABSTRACT

The report gives results of a review and analysis of the readily available information on total suspended particulates in the atmosphere. The purpose of the review was to determine the relative contribution of primary and secondary particulate matter to the total aerosol mass suspended in the atmosphere and to identify where the available information is insufficient to determine the needs for future control technology development. The report does not identify the fraction of total suspended particulates attributable to mobile and to stationary sources.

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TOTAL SUSPENDED PARTICULATES: REVIEW AND ANALYSIS

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1.0 INTRODUCTION

This report summarizes work done by Radian Corporation under EPA Contract No. 68-02-1319, Task 27. The study involved a review and analysis of the readily available information on total suspended particulates in the atmosphere. The purpose of this review was to determine the relative contribution of primary and secondary particulate matter to the total aerosol mass suspended in the atmosphere and to identify where the available information is insufficient to determine the needs for future control technology development. In addition, if possible, the fraction of total suspended particulates attributable to mobile and to stationary sources was to be identified. The work was performed from March through August 1975.

1.1 Background

The continental tropospheric aerosol consists of primary and secondary particulate matter which is emitted or is the result of emission from numerous natural and antropogenic sources. Primary particulate matter is any particulate matter that is emitted directly from a source and remains relatively unchanged chemically in the atmosphere. Secondary particulate matter is formed in the atmosphere from gaseous precursors. These gaseous precursors are generally "pollutant gases" (SO_2, NO_x, HC) emitted from many of the same sources as the primary particulate matter and also the gaseous constituents (NH_3) from natural sources, i.e., vegetation.

The aerosol mass suspended in the atmosphere varies in concentration, composition, and size distribution both as a function of time and location. This aerosol is normally divided into two mass fractions as a function of particle size. The "fine" fraction is usually defined as being the mass of particulates that have an aerodynamics diameter between 0.01 and 1.0 micron. The large particulate fraction roughly encompasses those particulates with an aerodynamic diameter of 1.0 to 100 microns. Existing ambient air quality standards do not distinguish between these two fractions although it is the "fine" fraction which is known to have the greatest impact on visibility in a region and is thought to cause adverse health effects. The visibility reduction is due to the scattering of light by particles in the submicron range while the potentially adverse health effects are due to the respirable nature of particles in this size range.

As much as three-fourths of the population of the United States is living in areas in which the levels of suspended particulate matters exceed the ambient air quality standards. These areas include both urban and rural environments. Current control strategies are directed at reduction of antropogenic primary source emissions through the installation of mechanical collectors, wet scrubbers, fabric filters, and electrostatic precipitators. The most efficient of these devices remove nearly all of the large primary particulates but still allow fines to be emitted to the atmosphere. With the exception of wet scrubbers, these control devices are incapable of achieving any control of secondary particulates.

Evidence is now accumulating which indicates that significant amounts of fine particulate matter may be secondary in nature. In some locations this secondary particulate matter may be the dominant fine particulate matter.

1.2 Objectives

The Industrial and Environmental Research Laboratory (IERL, formerly the Control Systems Laboratory) of EPA is reponsible for the development of technology for the control of pollutant emissions from stationary sources. Major research areas funded by IERL involve the development of improved control technology for sulfur dioxide, nitrogen oxides, hydrocarbon, and particulate emissions. In the area of particulate emission control, emphasis is being placed by IERL on the control of emissions of fine primary particulates. The direction of future particulate control technology development could be greatly impacted by evidence being accumulated for various regions by EPA and others, which indicates that the majority of the fine particulate matter suspended in the atmosphere is secondary. It is vital to the particulate control technology development program to determine if this evidence is accurate and applicable on a national scale. The objective of this short term study was to determine what data were available that could be used to assess the relative contributions of primary and secondary particulate matter to the atmospheric aerosol and to assess whether or not sufficient data existed to define future control technology needs for stationary sources.

In order to accomplish the objective stated above, Radian reviewed a small body of literature made available by EPA and contacted several experts in the field of atmospheric science to determine the current state of the art of their knowledge in the areas of interest.

1.3 Contents of the Report

The consultants used by Radian in the course of this study included: (1) G. M. Hidy and P. K. Mueller, Environmental Research and Technology, Inc., Westlake Village, California; (2) J. P. Lodge, Consultant in Atmospheric Chemistry, Boulder, Colorado; (3) J. R. Brock, University of Texas, Austin, Texas. These experts in the fields of aerosol characterization and atmospheric chemistry independently prepared reports incorporating their own knowledge and experience into interpretations of the data provided by EPA. A fourth consultant - L. R. Babcock, Jr., School of Public Health, University of Illinois, Chicago, Illinois - took these three reports plus a recent paper by Gartrell and Friedlander and interpreted each expert's findings in light of the others.

Radian utilized the output of each of the consultants, information gathered at a recent Gordon Research Conference and Radian in-house expertise to prepare this report. A brief summary of the results of the overall program is given in Section 2.0. The conclusions and recommendations are discussed in Section 3.0. Section 4.0 is the bibliography and contains the references provided by EPA as well as those used by each consultant. Section 5.0, the Appendix, contains the four reports generated by the consultants mentioned above. These reports constitute the body of this report. The interested reader should study these reports in their entirety.

2.0 SUMMARY

The results and discussion presented in this report are based upon the four input reports (included in the Appendix) discussed in the introduction and information obtained by Radian at a recent Gordon Research Conference. The significant results of each report and the information presented at the Gordon Research Conference are summarized below.

Each of the consultants reports prepared for this study approach the problem in a unique but meaningful way. Each report should be read in its entirety in order to gain each author's insight and perspective regarding atmospheric aerosol characterization and control.

2.1 Hidy and Mueller

This report emphasizes the California studies with which the authors are most familiar. Data on both chemical composition and particle size of atmospheric particulates is presented. The particle size data presented confirms the existence in the Los Angeles area aerosol of a bimodal mass distribution with respect to particle size. The chemical composition data presented represents an attempt to trace the source of atmospheric particulates.

The chemical tracer method of S. K. Friedlander and others is proposed by the authors as being the best available technique for tracing the sources of atmospheric aerosols. The results of Gartrell and Friedlander (later discussed in detail by Babcock) were discussed. Source species data for Pasadena and Pomona are presented and natural and antroprogenic sources of primary particulates are identified.

Material resulting from the oxidation of SO_2 and NO_x and condensation of non-methane hydrocarbon vapor was shown to contribute a substantial fraction of the total particulate mass concentration occurring in urban and non-urban air. While the authors indicated that this secondary aerosol could represent as much as 40-50% of the total aerosol in these areas, no attempt was made to assign sources for the secondary particulates. Hidy did append an earlier work, for which he was coauthor, which examined possible mechanisms for secondary particulate formation in the atmosphere.

2.2 Lodge

While Hidy and Mueller confined themselves mainly to the California experience, Lodge provided a wider viewpoint by discussing data obtained from urban Southern California, rural and urban Colorado, Chicago, and Milan, Italy. Based on the results of studies performed in each of these areas, Lodge agreed with Hidy and Mueller that secondary particulates could comprise as much as 40 percent of the total aerosol. However, Lodge warned against confusing the terms primary and secondary particulates with the terms large and fine size fraction, Lodge identified the material and antropogenic sources of both primary and secondary particulates and pointed out that primary particulates could be both large and fine and that while most secondary particles are fine the existence of large secondary particulates was possible. Lodge described conditions in Denver and rural Colorado during which nearly 90% of the atmospheric aerosol was observed to be larger than one micron and almost no secondary particulates could be identified. These results, obtained during the winter are completely counter to results obtained for Denver during the summer when the Denver aerosol closely resembles that found in Southern California.

Perhaps Lodge's most important contribution to this study was the important differentiation he made between contemporaneous carbon (that derived from recent biota) and carbon derived from fossil fuels. He concluded that "an important portion of the organic matter (in the ambient aerosol) consisted of spores, microorganisms, pollens and contaminated plant material". He did not assign a size fraction to this contemporaneous carbon. It should be noted however, if "contemporaneous carbon" were a generally present pollutant it would most likely all be in the large particle mode and would not be very soluble. As such, it would be observed in total C, H, and N analysis but not as a soluble organic. According to William Wilson of EPA most recent work has determined that organic material present in total particulate samples is soluble in various solvents.

2.3 Brock

This report provides a comprehensive review of both primary and secondary particulate matter, including both theoretical and empirical information. Brock basically supports the conclusions of Lodge as well as those of Hidy and Mueller. He states that on a global basis as much as 40% of the suspended particulate matter is secondary in nature (mostly sulfates, nitrates, and condensed hydrocarbons). Like the other consultants Brock makes an attempt to assess the sources of primary particulates. Brock's major contribution to this study was to provide estimates for 1970, 1980, 1990, and 2000 of the mass emission, particle size, and residence time in the atmosphere for emissions from 23 different source categories. Brock uses these data to show how particle size affects the relative contribution to aerosol mass. That is, that large sources of large particulates, such as crushed stone, contribute very little to aerosol mass, and that control of such sources will have very little effect on ambient aerosol mass.

2.4 Babcock

Babcock took the output of the three previously discussed reports plus a recent paper by Gartrell and Friedlander and attempted to determine source-characterization relationships for atmospheric aerosols. Two detailed source species size characterizations were performed, one for a composite of five California cities and a second that was chosen to be representative of nationwide emissions. Secondary particulates comprised a significant fraction in both characterizations.

Babcock's chief contribution to this program was to attempt, by extending the work of Gartrell and Friedlander and Brock, to determine what fraction of the fine particulates were primary particulates. Babcock had to make a large number of assumptions to accomplish this goal, however the results are most interesting as they indicate that as much as 16% of the total atmospheric aerosol may consist of fine primary particulates from stationary sources. Babcock also indicated that 26-49 percent of the total suspended particulates in the atmosphere were from stationary combustion and other industrial sources.

2.5 Gordon Research Conference

An Environmental Sciences: Air conference was held August 18-22, 1975 at the Gordon Research Center, New Hampton, New Hampshire. The topic of this conference was fine particulate matter (0.01-1.0μ) in the troposphere. The majority of the contributors to this study as well as other experts in this field and other interested parties attended. The areas of interest to this study – mainly the size, mass, and composition of fine particles in the troposphere – were discussed at length at this conference.

No data counter to that presented by the four consultants utilized in this study was presented. However, indications were given that sampling and analytical procedures used to date to gather data on the size distribution and chemical composition of atmospheric aerosol may be biased. Much of the sulfate and nitrate data gathered to date from hi-vol filter samples may be erroneously high. This would mean that the contribution of secondary particulates to the total aerosol mass may be much less than previously suspected. This problem is mainly one of conversion of gases in the atmosphere to particulates on the filter due to the chemical and physical properties of the filter media used and the meteorological conditions (particularly humidity) at the time the sample was taken.

While no one at the conference seriously questioned the multimodel nature of the mass distribution of suspended particulates with respect to size, there was no agreement on a good method of determining particle size distribution. Each method has its problems. When it is desired to separate size fractions for chemical analysis, the problem becomes compounded because of such diverse factors as particle bounce and condensation. It was pointed out that large particles have been observed to bounce from one stage of an inertial impactor to another thus giving distributions unfairly biased toward the fine fraction. Condensation and or crystallization of new particulates from gaseous material passing through particle sizing devices was demonstrated to give significantly erroneous chemical compositions.

Elemental analysis tracer studies were also discussed. These studies utilized techniques that were much the same as those discussed by Hidy and Mueller. The drawbacks associated with this type approach were discussed and the need for chemical compound identification in place of elemental identification was demonstrated. Without such techniques it is difficult to distinguish between particulate matter such as coal ash and soil.

Two of the most important things noted by this author at the conference were the extent to which the whole body of knowledge in this area is built upon the California experience and the in-breeding among the experts in the field. There seems to be a definite need for additional data on other regions of the country and for fresh ideas and inputs into studies in this area.

3.0 CONCLUSIONS AND RECOMMENDATIONS

The California data currently available indicates that material resulting from the oxidation of SO_2 and NO_x and condensation of non-methane hydrocarbon vapor appears to contribute a substantial fraction of the total particulate mass concentration in both urban and non-urban air. A few cases have been observed in Southern California where more than half the sampled particulates were secondary. These secondary particles were heavily concentrated in the submicron particle range.

For Denver and rural Colorado, during a significant fraction of the year, nearly 90% of the atmospheric aerosol was primary and concentrated in the large fraction (greater than 1m). This was true even though the total mass concentration of suspended particulates was approximately equal to that observed in Southern California.

Source characterization studies performed or cited by the various consultants do a credible job of identifying the sources of primary particulates larger than one micron. From these studies it is evident that natural or quasi-natural sources are significant contributors to the primary aerosol mass (primarily fugitive dust, sea salt, and pollen).

The identification of the sources of secondary particulates was not attempted by most of the experts involved in the study. Current knowledge of the mechanisms and rates of conversion of gases and vapors to aerosols was believed by the majority of the consultants to be inadequate at the present time. The one consultant, L. R. Babcock, who attempted to trace sources of secondary particulates through a series of assumptions, found that stationary combustion and industrial sources were the major anthropogenic sources of atmospheric aerosol. While mobile sources were a significant problem in Babcock's source-species-size characterizations they were not the dominant category even for California. Babcock felt that the ranges presented in his study might bound the problem, thus assessing the contribution of fine primary particulate emissions at somewhere between 4 and 16 percent of the total suspended aerosol mass on a national basis.

Better definition of real problem areas such as the concentration of particulates in each size range and better analytical data on the compositions of particles in those size ranges is definitely required before the true nature of the atmospheric aerosol problem can be understood. It is clear that there is no single generalized source-species-size characterization which is applicable throughout the nation. The various distributions may all tend toward bimodal, but the sources and species appear to vary significantly from location to location, depending on local sources. Adding further complexity, the relationship between sources and ambient air quality seems to vary significantly from season to season and even hour to hour. The incomplete distributions published to date are probably not representative of their own regions, much less of the nation as a whole.

The fact that significant amounts of aerosol may be derived ultimately from pollutant gases places potentially important and new constraints on control strategy for aerosols. It is now recognized that control of fine particle emissions in the 0.1 to 1 μm diameter range at the source is crucial for achieving improved air quality for public health. Even though these particles may include only a part of the total mass concentration, they are important for development of respiratory ailments and remain in the atmosphere the longest. The fine particle control problem is compounded by the addition of condensable material formed following atmospheric chemical reactions. On the basis of this study, it would appear that the research programs sponsored by IERL which are being directed toward improved control of sulfur oxide, nitrogen oxides, and hydrocarbon emissions, may play a large role in helping to control the levels of submicron suspended particulates in the atmosphere. In addition, it would appear that a continued program to find methods of improving control of fine primary particulates from stationary sources is justified.

As a result of the work performed by Radian and each of the expert consultants employed in this study, it is recommended that:

1) The chemical element balance method for identifying the origins of aerosols be applied to several cases in diverse areas of the United States to confirm the importance of secondary processes in aerosol production and to separate man-made from natural secondary aerosol sources.

2) Better means of chemical analysis be developed so that chemical compounds rather than elements can be used to identify major sources.

3) Research into secondary aerosol formation to determine the mechanisms and rates of conversion of gases and vapors to aerosol should receive high priority. This information, which is currently inadequate, will be required to determine the degree of control of pollutant gas emissions that will be required for secondary particulate control.

4) Existing data on nitrate and sulfate particulates should be reassessed in light of recent work done by EPA and the Electric Power Research Institute on the formation of artifact sulfates and nitrates during filtering of atmospheric aerosol.

5) The present programs underway at IERL to improve control of sulfur oxides, nitrogen oxides, and hydrocarbons should be continued as these pollutants can play a large role in the formation of fine secondary particulates in the atmosphere.

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CONTROL TECHNOLOGY AND AEROSOLS

ERT REPORT P-1588.F
MAY 1975

by

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&

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SUMMARY AND RECOMMENDATIONS

This report gives a brief literature survey of the work undertaken recently to characterize atmospheric aerosols in terms of their origins. Particles come directly from stationary or mobile sources, or from the production of condensed material by chemical reactions taking place in the ambient air. Material resulting from the oxidation of SO_2, NO_x and non-methane hydrocarbon vapor appears to contribute a substantial fraction of the total particulate mass concentration occurring in urban and non-urban air. A few cases have been observed in Southern California when more than half of the sampled particles stemmed from atmospheric reactions. This material is concentrated in the submicron particle size range. The formation of particles in the atmosphere from pollutant gases requires new perspectives for controlling such materials, which must be taken into account in future strategic planning.

It is recommended that:

1. The chemical element balance method for identifying the origins of aerosols be applied to several cases in diverse areas of the United States to confirm the importance of secondary processes in aerosol production and to separate man-made from natural secondary aerosol sources.

2. Present control strategies for particulates be reconsidered to include the impact of the conversion of SO_2, NO_x and non-methane hydrocarbon vapors into condensed material.

3. To achieve the above recommendation, a substantial amount of observational data is still needed for the major urban regions. Studies are also needed to test the evaluations made so far for the Los Angeles region.

1.0 INTRODUCTION

This report has been prepared in response to a request from the Environmental Protection Agency's (EPA) Control Systems Laboratory. According to evidence from recent work characterizing aerosols, a major fraction of the particles originates from atmospheric chemical processes. Some studies suggest that these "secondary" generation mechanisms dominate the particulate mass concentration compared with "primary" emissions from sources. This conclusion is of considerable importance in determining the future requirements of control technology to meet present ambient air quality standards.

To assist EPA in the assessment of current control procedures, Radian Corporation has solicited information from several investigators on the available studies of major atmospheric particle sources. Findings of recent studies are discussed in this report. Some of the work was sponsored partially or entirely by EPA. This effort is evaluated with respect to future needs in particulate control technology at the source, and recommendations are presented that take into account atmospheric chemistry.

2.0 CHARACTERIZATION OF PARTICLES

During the last decade, considerable information has been collected on the physical and chemical properties of urban and non-urban aerosol particles for urban and non-urban air. The suspended particles are composed of a wide variety of solid and liquid material. Some of the particles are polycrystalline and appear to be soil dust or other kinds of solids resulting from comminution processes. Other solid particles are amorphous spheroids which are identified with combustion processes or with condensation of vapor in the atmosphere. Liquids are frequently seen in atmospheric aerosol samples, especially in the submicron particle size range.

Investigations such as those of Whitby et al (1972) have established that aerosol particles range in size from less than 100 Å to several 10's of micrometers (μm) in diameter. The size distribution of particulate surface area and volume is multimodal in character; the most commonly observed volume distributions are bimodal, with one mode peaking in the range between 1 and 10 μm diameter. An example of such distributions is shown for Los Angeles air in Fig. 1. Evidence from prior observations showing similar distributions are shown in Fig. 2. Here V is particle volume and D_p is particle diameter. The volume distribution is approximately proportional to the mass distribution.

Recent experiments such as those in the California Aerosol Characterization Experiment (ACHEX) (e.g., Hidy et al, 1974) have shown the behavior of the submicron and supermicron modes to be essentially independent. The supermicron particle grouping appears to be dominated largely by wind-blown dust, sea salt, road dust, construction dust, and other debris from comminution processes. The submicron range appears to be related principally to primary emissions from the burning of fossil fuels and to the secondary particulate production of condensable material in the atmosphere. (See, for example, Heisler et al, 1973; Hidy and Burton, 1975; Gartrell et al, 1975). The latter process is especially dramatic in cities such as Los Angeles, where chemical reactions are a dominant force in the evolution of smog aerosol (Hidy et al, 1974). An example of the changes due to particle growth during smog reactions and air mass transport is shown for Pomona, CA in Fig. 3. The fraction of aerosol volume increased substantially between early morning and mid-morning. The major accumulation of aerosol volume in air moving over the fixed station takes place in the submicron size range, while the supermicron range remains essentially the same. Up to now, this phenomenon is poorly documented except partially for Denver (Willeke, Whitby et al, 1974; Durham, Wilson et al, 1975; Durham, Patterson et al, 1975). Currently active EPA sponsored studies (W.E. Wilson) for the St. Louis region

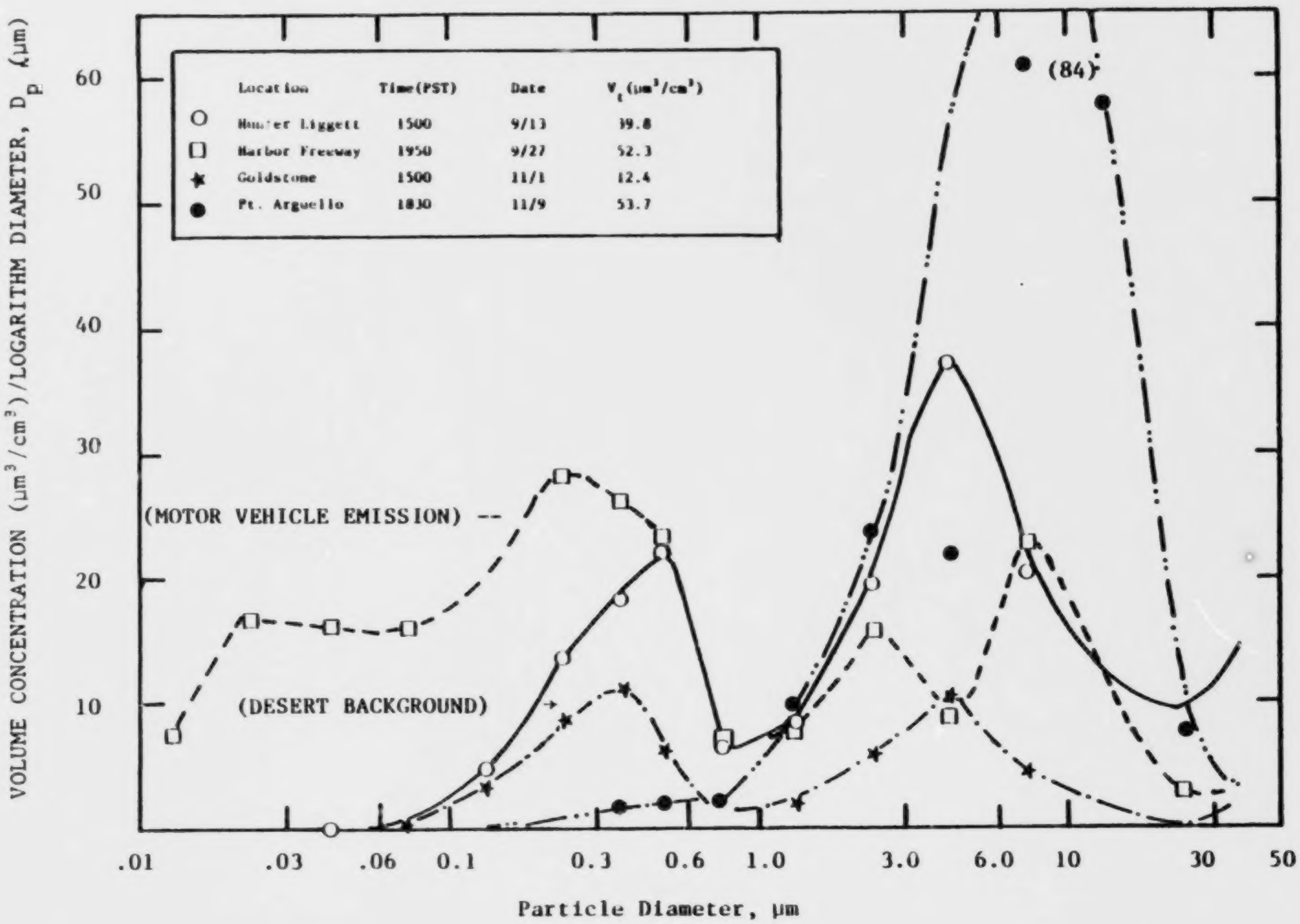

Figure 1. Comparison of Volume Distributions for Background and Motor Vehicle Source Enriched (Near Harbor Freeway) Sites. V_t is the Total Volume Concentration of Aerosol, as estimated from the particle counters. Data taken in 1972.

Source: Hidy, et al, 1975: Characterization of Aerosols in California, Vol. 1, California Air Resources Board Contract No. 358, Rockwell International Science Center, Thousand Oaks, CA.

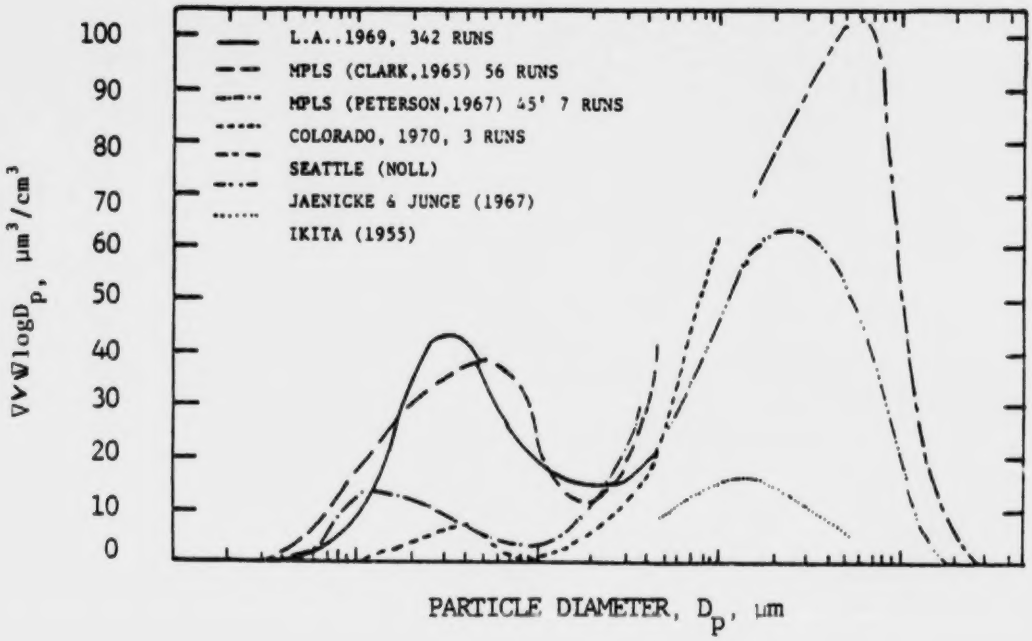

Figure 2. Comparison of volume distributions measured by several investigators in different locations. Note the universal bimodal nature of all of these data and that the data obtained by Clark, Peterson, and from the more recent Los Angeles and Colorado studies, all fall into the Jaenicke and Junge and Noll data at about 7 μm. Also note that the Colorado data which were obtained under pollution-free conditions such that it may be assumed that a background aerosol was being measured, is rising sharply at 10 μm.

Source: Whitby et al, "The Aerosol Size Distribution in Los Angeles Smog", Aerosols & Atmos. Chem. (G.M. Hidy, ed.). Academic press, N.Y., p. 260.

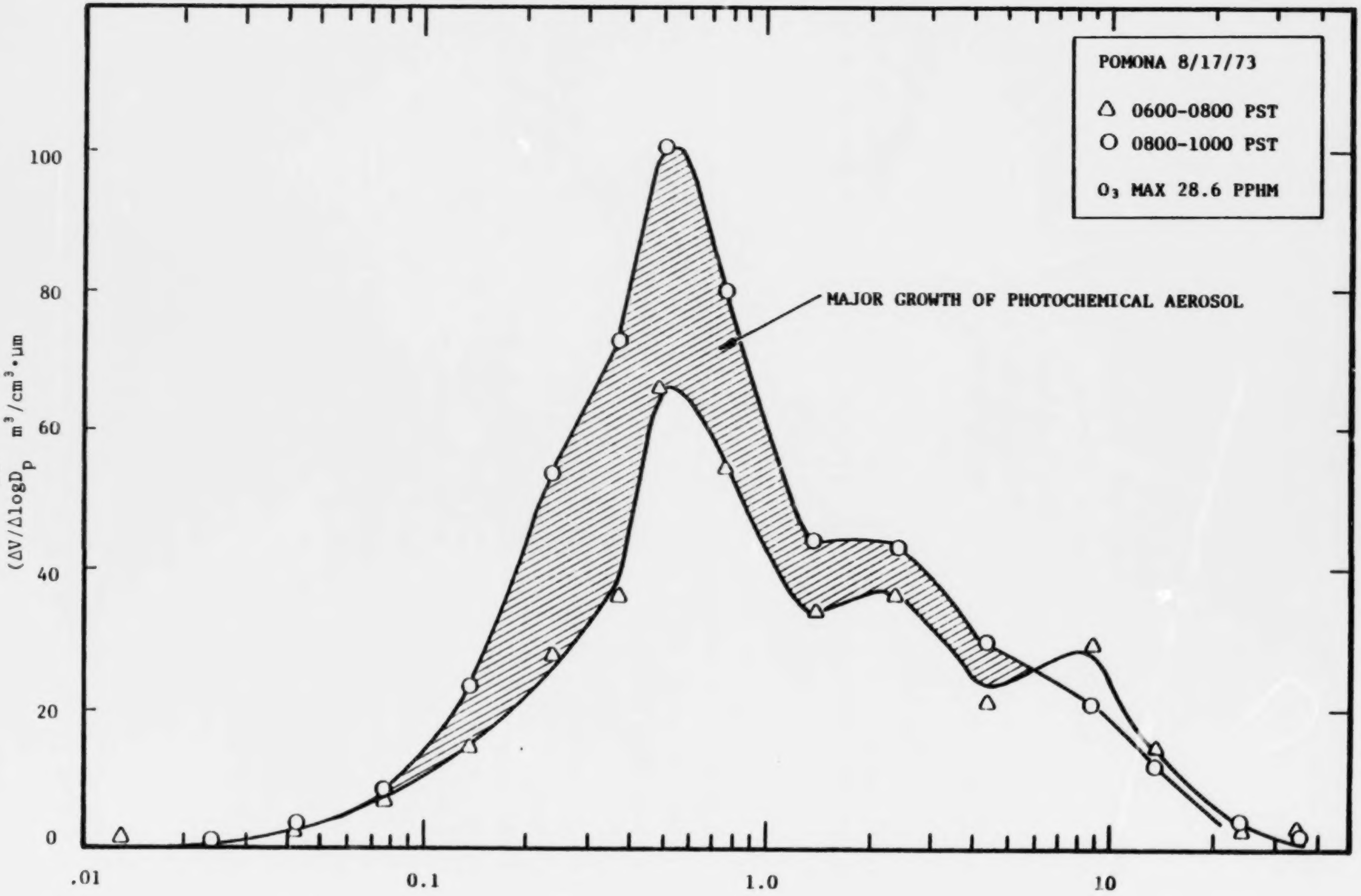

Figure 3. Evolution of the Volume Distribution of Smog Aerosol Taken at Pomona, CA 8/17/73.

Source: Hidy et al,1975: "Characterization of Aerosols in California, Vol. 1, California Air Resources Board Contract No. 358, Rockwell International Science Center, Thousand Oaks, CA.

will test the occurrence of these types of changes further. No preliminary data from these studies have as yet been available to ERT.

The data shown in Figs. 1 to 3 indicate the great importance of taking into account the wide range of particle size and the behavior of certain parts of the size spectrum in response to primary sources as well as atmospheric chemical processes. Since both human respiratory responses and visibility are linked primarily with the submicron or fine particle size mode, control efforts should be focussed on those materials.

The chemical properties of aerosols provide important additional information about the nature and origins of the particles. The atmospheric aerosol is composed of a very wide range of both inorganic and organic material.

Examples of the chemical composition of urban and non-urban samples taken in California are shown in Table 1. Although several elements and species are identified in these samples, the material is dominated by carbon (water soluble sulfate), water soluble nitrate, and ammonium. There is a large body of data on aerosol composition available from the National Air Surveillance Network and special studies which suggest that these four components make up a major fraction of aerosols sampled in the United States. Thus, the California experience should be applicable qualitatively to other locations.

Attempts have been made recently to establish a total material balance on filter collected aerosol particle samples (e.g., Hidy and Friedlander, 1971; Miller et al, 1972; Heisler et al, 1973; and Gatz, 1975). Using the chemical analysis of samples and certain assumptions about the composition, all except 20 to 30% of the total collected mass can be accounted for. Such calculations have confirmed that sulfate, nitrate and non-carbonate carbon are major contributors to the mass of aerosol. These materials must have originated from atmospheric chemical processes since they are not accounted for by emissions from known primary sources.

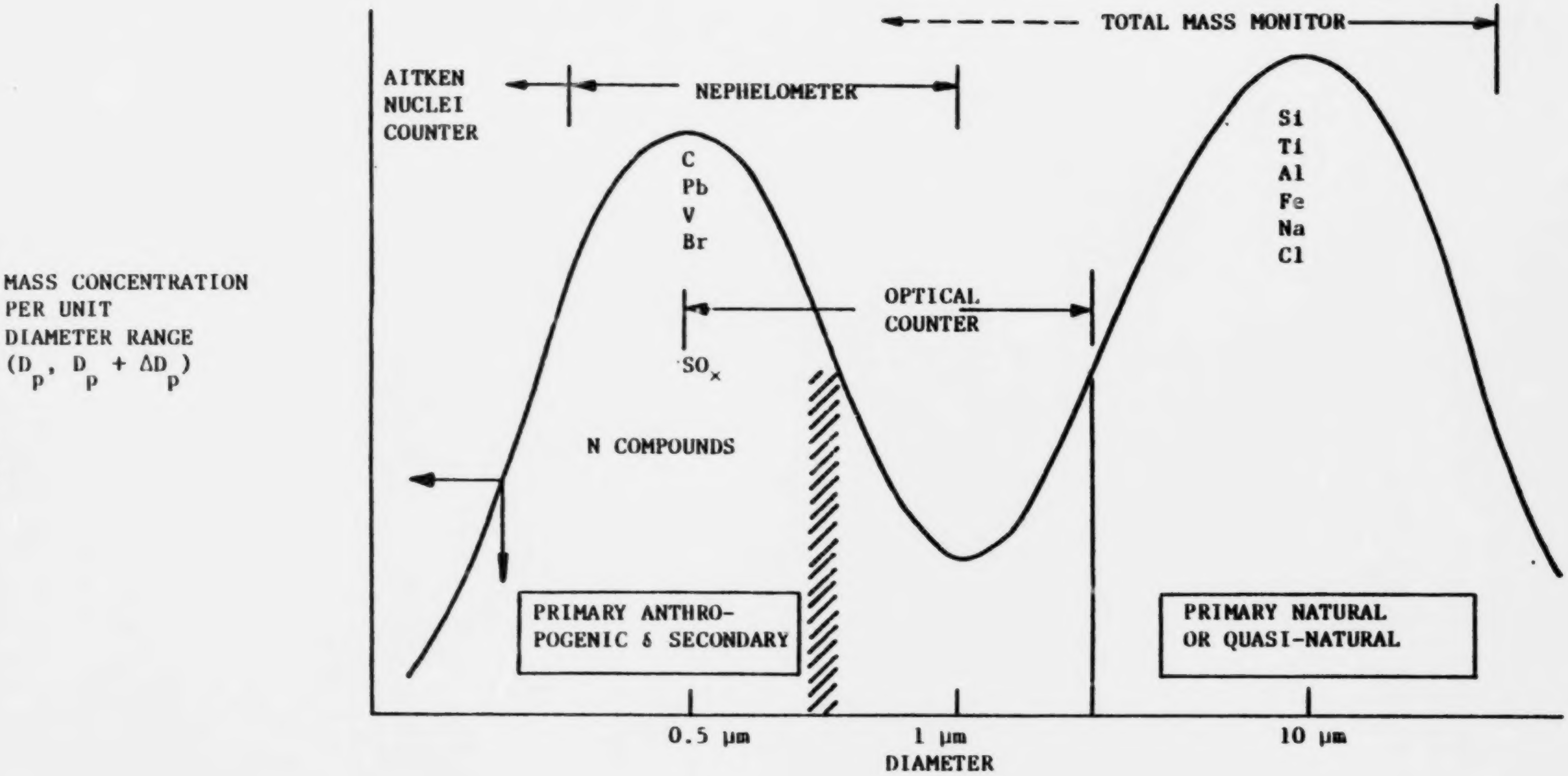

Figure 4. Hypothetical Presentation of Bimodal Mass Distribution Based on Work on Urban Aerosols through 1971.

Source: Hidy, et al, 1974: "Characterization of Aerosols in California", Volume 4, Calif. Air Resources Board Contract No. 358, Rockwell International Science Center Report SC524.25FR, Thousand Oaks, California 91360.

Table 1

Chemical Composition of Filter Collected Aerosol Samples

Constituent	Weight Percent			
	Non-Urban		Urban	
	Pacific Coast* Offshore	Desert+	Fresno+	Pomona+
Al	2.8	2.4	2.4	0.99
Si	5.0	5.2	6.3	2.2
Na	3.6	0.71	0.40	1.1
Cl	9.9	0.32	0.19	0.51
K	1.3	0.39	0.33	0.24
Ca	1.9	2.1	0.47	1.0
Ti	0.15	0.13	0.09	0.11
V	N.D.	0.004	N.D.	0.008
Cr	0.02	N.D.	0.0058	0.013
Mn	0.04	0.028	0.025	0.025
Fe	1.6	1.4	1.03	0.86
Cu	0.6	0.028	0.0058	0.014
Zn	0.2	0.035	0.055	0.13
Br	0.2	0.059	0.098	0.36
PB	0.4	0.017	0.42	1.6
I	-	-	-	-
$SO_4^=$	17.5	2.8	2.0	10.6
NO_3^-	5.7	3.5	3.8	20.2
NH_4^+	2.2	1.7	1.5	9.1
Non Carb. C	3.0	N.D.**	5.0++	24.0++
Total measured (g/m^3)	30	42.4	207	180

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*Average of 20 samples at San Nicolas Island (Hidy et al., 1973)
+Single 24-hour sample (Hidy et al., 1974)
++Estimated as 3 x cyclohexane extractable organics
**Not detected

Source: Hidy, G. M. & C. S. Burton, 1975: "Atmospheric Aerosol Formation by Chemical Reactions", presented at Sym. Chem. Kinetcis for Lower & Upper Atmos., Warrenton, VA., Sept. 1974.

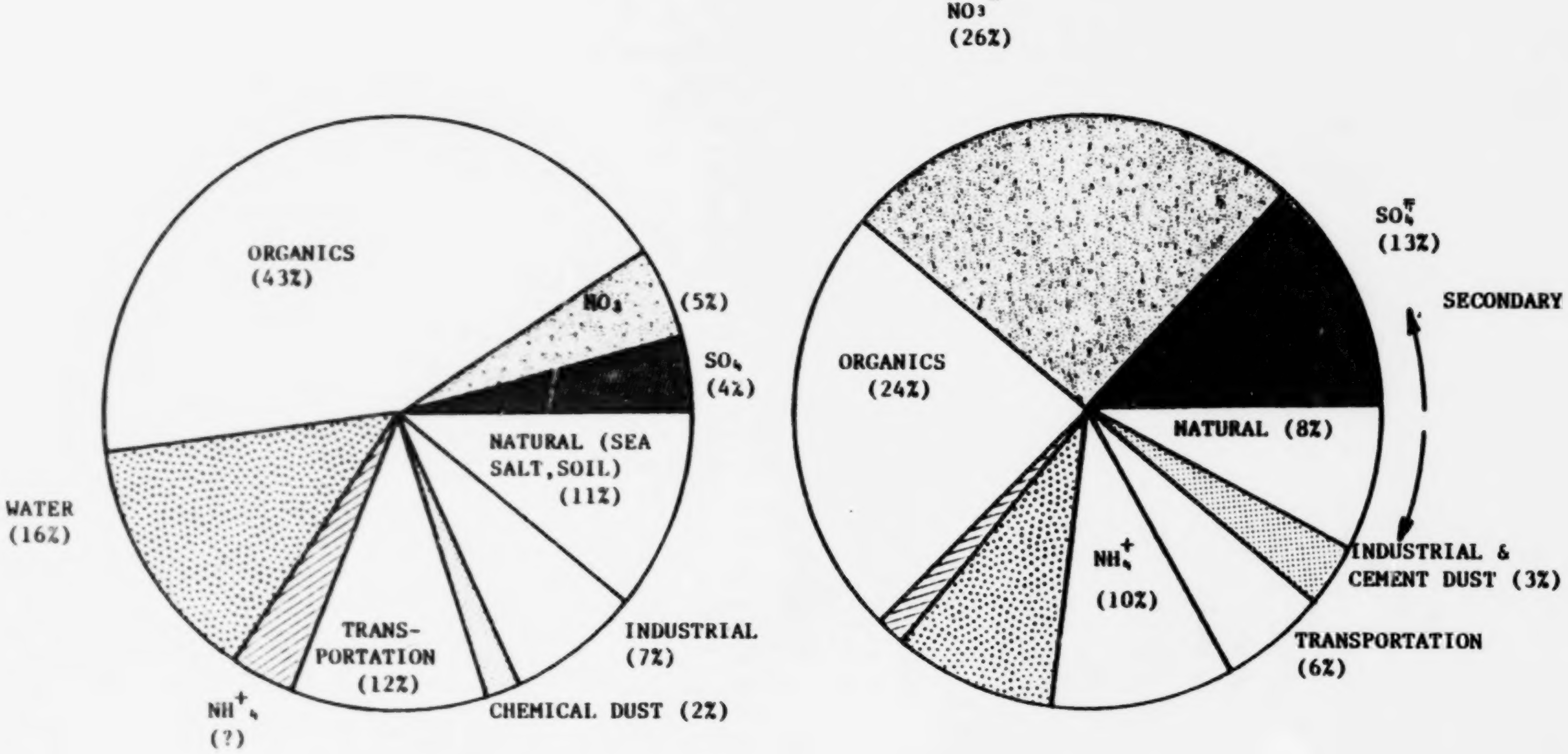
Microscopic analysis has been developed through the work of McCrone and others and has been used recently by Draftz and colleagues to identify the origin of large, solid particles sampled in Denver and in the Chicago area. Filter and impactor samples have been examined by polarized light microscopy after treating the filter substrate with immersion oil. This method is useful in characterizing particles but suffers from the severe limitation that it can be used only for solid, insoluble (in immersion oil) particles larger than 0.5 μm diameter. As a result, the discussions of source characterization by Draftz and Durham (1975) (also Harrison et al, 1975) do not include the fine particle range where secondary material may be expected. Their conclusions that most of the sampled material is primary in origin is based on a partial "material balance" and cannot be considered to provide a complete picture of the contribution of primary or secondary sources to atmospheric aerosol.

Methods for electron microscopic identification of particles were developed by Frank & Lodge (1967). Their work was particularly useful in characterizing particles such as sulfuric acid and sodium chloride. Such investigations have provided useful information about the origins of aerosols, especially from volcanoes. But this technique is difficult to implement quantitatively.

The second method is to "fingerprint" sources of aerosols by interpretation of changes in size distributions with time. The group at the University of Minnesota has catalogued a large number of size distributions taken near individual sources in an attempt to find unique patterns. So far the work has indicated that blowing soil dust and strong combustion sources can be identified. Air mass trajectory and chemical information is required in addition to relate the source contributions to various size fractions observed in the ambient air.

The third method utilizes the chemical composition of aerosol particles collected on a substrate by relating the composition to components which are virtually unique for major sources. (See, for example, Hidy & Friedlander, 1971; Miller et al, 1972; Friedlander, 1972; Heisler et al, 1973; and Gartrell & Friedlander, 1975.) Examples of chemical tracers include lead for automobiles, sodium for sea salt and soil dust, silicon for soil dust, vanadium for fuel oil, etc. The source identification can be made in broad classes using such tracers and an emission inventory for a city. The method has been applied to the particulate matter found in Los Angeles. A typical breakdown by sources is shown for non-smoggy and smoggy conditions in Figs. 5A and 5B. The primary emissions account for less than half of the total mass concentration in air over this city. The secondary contributors of sulfate, nitrate, organic carbon, ammonium and water encompass the remainder of the sample. These components are substantially increased during the smoggy conditions.

A similar analysis has been made for aerosols sampled at a remote island site approximately 90 miles west of Los Angeles. The estimated breakdown by source for non-urban material offshore is listed in Table II. Even in this case the major part of the material appears to be attributable to secondary reactions of the pollutant or quasi-pollutant gases, SO_2, NO_x, NH_3 and hydrocarbon vapors. Analogous preliminary chemical information has become available for a Bermuda aerosol sample (Akselsson et al, 1975.) Utilizing a novel approach, particles are collected as a function of size on five cascade impactor stages and are analyzed by proton elastic scattering (PESA) and proton induced X-ray emissions (PIXE). PESA obtains C, O, N and S in the sample while PIXE obtains the higher atomic number elements. The carbon was most abundant, 25 to 30 $\mu g/m^3$. The ratios of S, N, and O were consistent with that expected for $(NH_4)_2\ SO_4$. The data published to date is not sufficient for detailed interpretation. An estimated excess observed in the nitrogen fraction suggests also the presence of some nitrate. In view of these findings at a remote location, it becomes important to find ways for allocating separately the anthropogenic and non-man made contributions to the secondary aerosol.



A. PASADENA 9/20/72
1200-1400 PST
LOW OXIDENT, TOTAL MASS
CONCENTRATION, 79 μg/m^3

B. POMONA 10/24/72
1200-1400 PST
MODERATE OXIDANT, TOTAL
MASS CONCENTRATION, 178 μg/m^3

Figure 5. Distribution by Source of Aerosol Mass Concentration for Filter Samples Collected Over Two-Hour Periods, and Equilibrated to Air at Less Than 50% Relative Humidity.

Source: Hidy et al, 1975: "Characterization of Aerosols in California, Vol. 1, California Air Resources Board Contract No. 358, Rockwell International Science Center, Thousand Oaks, CA.

TABLE II

CONTRIBUTION BY SOURCE TO SNI AEROSOLS (WEIGHT PERCENT)

1. Primary	Soil (based on 25% Si in soil)	20.0
	Sea salt (based on 30.6% Na in sea salt)	11.1
	Automobile lead (based on 40% lead in auto emitted aerosol)	1.0
	Carbon*	3
2. Secondary	Sulfate	17.5
	Ammonium	2.2
	Nitrate	5.7
		61
3. Total volatiles other than carbon: 100 - (Total ash carbon)		22
	Total accounted for	83

*Some of this may be produced in the atmosphere by chemical reaction; however, it is identified with primary origin for this estimate.

Source: Hidy et al, 1974: "Observations of Aerosols over Southern California Coastal Waters", J. of Appl. Meteror. Vol. 13, pp. 96-107.

The chemical element balance approach has been used by Harrizon & Winchester (1971) for analysis of sources for the Chicago area. Sources were identified, but the chemical analysis was insufficient to deduce the significance of secondary processes in that city. Gatz (1974) has recently reported a similar analysis for aerosols sampled in St. Louis. Although the data again suggest the important contribution of sulfate and nitrate to the aerosol, the non-carbon constituent was unavailable to complete the material-source balance.

Several years ago, the calculation method of Hidy & Friedlander (1971) was applied to National Air Surveillance Network data for several cities, including Philadelphia; New York; Washington, D.C. and St. Louis. These calculations were undertaken by EPA staff and resulted in an internal Agency document which is not currently available. Friedlander was involved in this study and may have a copy. In any case, the results of such calculations appeared to show the importance of the "secondary" constituents, sulfate, nitrate and organic carbon, as a major contributor to aerosol mass concentration in the cities considered.

On a global basis, Hidy & Brock (1971) estimated that the secondary particles formed by atmospheric chemical reactions of SO_2, NO_x and hydrocarbon vapor would be dominant in the worldwide aerosol. The calculations were based on considerations similar to those introduced by Hidy and Friedlander (1971).

The chemical element balance approach was extended recently to estimate the relative contributions of various sources to the secondary part of the ambient aerosol. White et al (see also Hidy et al, 1974) segregated two major categories -- stationary (fuel oil) and mobile (gasoline) combustion sources in the Los Angeles Air Basin. From the emission inventory for the city and atmospheric data obtained in the Aerosol Characterization Experiment, the contribution from these sources to the aerosol mass concentrations were calculated. The results are shown graphically for different locations in Fig. 6. Stationary sources were more important total contributors to the aerosol in the western and central part of the Basin than in the eastern area.

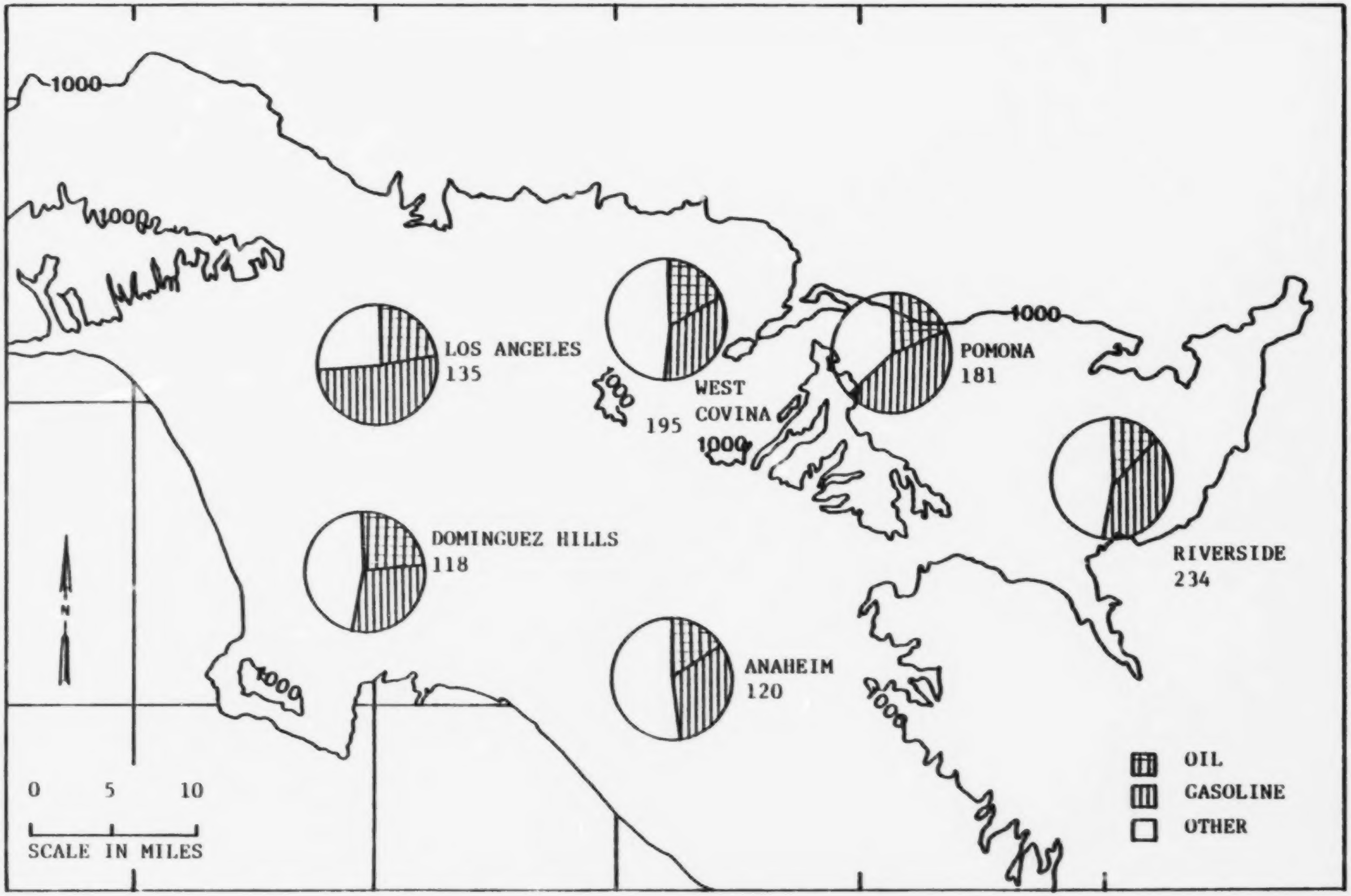

1000
1000
LOS ANGELES
135
WEST
COVINA
195
POMONA
181
RIVERSIDE
234
DOMINGUEZ HILLS
118
ANAHEIM
120
N
0
5
10
SCALE IN MILES
OIL
GASOLINE
OTHER

Figure 6. Distribution of Sources for Aerosol Mass Concentration in the South Coast Air Basin. Numbers by Discs are Averaged Mass Concentrations of 2-hour 1973 samples. The Contour is the 1000 ft. height level.

Source: Hidy, et al, 1975: "Characterization of Aerosols in California, Vol. 1, California Air Resources Board Contract No. 358, Rockwell Intl. Science Center, Thousand Oaks, Ca.

The contributions to particulate loadings from the oxidation of SO_2, NO_x and hydrocarbon vapors is expected from their chemistry. The known chemistry about aerosol evolution was recently reviewed by Hidy & Burton (1975, Appendix). They showed several plausible pathways for the formation of condensed material by atmospheric chemical reactions. These reactions may be homogeneous-gas phase or heterogeneous; the latter involve particles and hydrometeors.

All of the discussion dealing with the filter or impactor sample collection and subsequent chemical analysis assume that current methods reflect "real" particle properties as they exist suspended in the atmosphere. There are significant uncertainties in current sampling methods which have been documented recently. Some of these, such as particle bouncing in impactors and loss of water, can be minimized. Other effects such as the influence of reactive gases, NO_x or SO_2, on particles collected on a substrate, or on the substrate itself, are currently being investigated. Some of the methods used in the past may have yielded suspect data and interpretations because the magnitude of possible collection and chemical analysis errors remain uncertain. The ACHEX work was conducted with such problems in mind (see Hidy et al, 1974). However, further developments in sampling and chemical analysis methods are needed to obtain a much improved data base.

Of the three methods for identifying particulate sources, the chemical element balance appears to offer the most promising basis for clues to the origins of the atmospheric aerosol. So far, it has been applied in complete form only to samples collected in Southern California. The method requires (1) detailed knowledge of the particulate chemical composition, (2) emissions inventories, and (3) some knowledge of chemical species from primary and secondary sources. Further use of the method should be made to investigate aerosol behavior in diverse areas of the United States to check the universality of the conclusion that secondary particle production can account for a large fraction of the particulate mass.

4.0 IMPLICATION TO CONTROL TECHNOLOGY

Even with uncertainties, it is evident circumstantially that chemical processes generating condensed material in the atmosphere provide a major fraction of the ambient aerosol concentration. In some cases, it appears that such material can account for much more than half of the total mass concentration of particles.

The material from secondary production includes water soluble sulfate and nitrate, non-carbonate (organic) carbon and ammonium. These are derived from atmospheric reactions involving the gaseous precursors, SO_2, NO_x, (non-methane) hydrocarbon vapor and ammonia.

Because significant amounts of aerosol are derived ultimately from pollutant gases, it places potentially important and new constraints on control strategy for aerosols. It is now recognized that control of fine particle emissions in the 0.1 to 1 μm diameter range at the source is crucial for achieving improved air quality for public health. Even though these particles may include only a part of the total mass concentration, they are important for development of respiratory ailments and remain in the atmosphere the longest (see also Hidy, 1973). The fine particle control problem is compounded by the addition of condensable material formed following atmospheric chemical reactions. The natural background component of the secondary aerosol remains to be assessed. For the Los Angeles Region, the annual background for all suspended particulate matter has been estimated at about 4.0 $\mu g/m^3$ (Trijonis, 1974). SO_2, NO_x, and hydrocarbon vapor from stationary and mobile sources in the light of expected aerosol production.

Proposed control strategies for the anthropogenic aerosol were calculated by roll-back from a base year and assumed a linear function to relate SO_2, NO_x and reactive hydrocarbon emissions to sulfates, nitrates and secondary organics respectively (Trijonis, 1974). Apparently, this approach is being extended to other regions with current EPA sponsorship. Hidy et al (1974) made similar assumptions but modulated the impact on both total mass (TSP) and visibility (^{b}scat) by considering the interactions which were observed during relatively severe pollution episodes. The following equations were derived statistically:

$$\text{TSP } (\mu g/m^3) = 26 + 1.56\ (NO_3^-) + (1.28 - 0.58\ \mu^2)\ (SO_4^=) + 2.55\ (\text{organics}) \pm 21,$$

and

$$b_{scat} \times 10^4 (m^{-1}) = -1.1 + 0.074\ (SO_4^=) + (0.025 + 0.049\ \mu^2)\ (NO_3^-) + 0.025\ (\text{organics})$$
$$+\ 0.025\ (\text{Mass} - SO_4^= - NO_3^- - \text{organics}) \pm 0.9$$

where constituent concentrations are given in $\mu g/m^3$ and μ is the relative humidity.

An analogous correlation was obtained by Barone, Cahill et al (1975) for a more extensive set of measurements. Their correlation relates composition to prevailing visibility. Elements and gas phase components including water vapor and wind speed were unfortunately omitted. While this type of correlative analysis of available data has the potential for more realistic evaluation of control strategies than linear roll-back alone, their sensitivities and applicability for different regions and time spans remain to be evaluated. A thorough analysis and substantially more observational data are still needed to estimate the required reductions in gaseous emissions to achieve the ambient aerosol standard. With such information as a base, strategies for control of major sources could be developed for given AQCR's.

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APPENDIX FOR
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52a

ATMOSPHERIC AEROSOL FORMATION BY CHEMICAL REACTIONS

by

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ABSTRACT

This paper is a review of several aspects of aerosol formation processes that occur in the Earth's atmosphere. Important contributors to atmospheric aerosol chemistry are the sulfates, nitrates, and organic compounds, which are considered to be formed mainly by reactions of trace reactive gases in air. The phenomenology of the evolution of aerosols by such chemical processes is illustrated by recent observations taken in Los Angeles smog. The results of this program show the strong relationships between sulfate, nitrate, and organic carbon formation and gas phase processes of photochemical smog.

Suspected mechanisms of secondary aerosol production are summarized, with consideration for both homogeneous and heterogeneous processes. These mechanisms are examined in the light of laboratory simulations and the knowledge of atmospheric behavior to deduce the potential importance of certain classes of reactions for explaining aerosol evolution. Such considerations illustrate well the complexities of gas-particle interactions in atmospheric chemistry.

1. INTRODUCTION

Over the past century, hundreds of studies have been made on visibility reduction in the atmosphere which are associated with aerosols making up haze. It has been known for sometime that haze involves the light scattering from tiny submicron particles suspended in air. Yet only recently has there been widespread recognition that such particles play an active role in air chemistry. Through their production and growth, workers have come to link them with the atmospheric removal of certain reactive gases such as the sulphur and nitrogen oxides and hydrocarbon vapors. The chemical mechanisms of aerosol formation in the atmosphere remain uncertain, but it is likely that many processes play a role, including important photochemical reactions.

Since Tyndall's 19th century classical experiments on aerosol optical behavior, it has been known that exposure of reactive gases to light can produce copious quantities of airborne particles. More recent observations have led investigators to believe that sunlight induced chemical reactions are responsible for a substantial fraction of the intense haze observed over cities such as those in Southern California. The relation between haze and photochemical reactions in polluted air was deduced many years ago from the work of Haagen-Smit and co-workers, and photochemical aerosol production was explored by many investigators including Stephens, Hanst, Renzetti, and Doyle (e.g., Leighton (1)). The possibility of widespread haze formation by sunlight induced reaction of background nitrogen oxides and natural terpenoid compounds from vegetation was suggested several years ago by Went (2). Recent research on the stratospheric aerosol has indicated that the major constituent by mass or airborne particles at high altitude is sulfur. One explanation for the presence of such material is via oxidation of traces of sulfur dioxide above the troposphere (e.g., Friend et al. (3)).

With increasing concern for the influence of man's activities on the atmosphere, there is interest in improving the air quality levels for aerosols generated from atmospheric pollutants. Thus there has been a substantial increase in research activity devoted to atmospheric aerosol chemistry, particularly photochemistry. At the same time that a variety of new laboratory experiments have been updated, major new field studies have been implemented to characterize atmospheric haze formation in more detail. Perhaps best documented of these is the 1969 Pasadena Smog Aerosol Study, whose methods and results were reported respectively by Whitby et al. (4) and in the volume, Aerosols & Atmospheric Chemistry, edited by Hidy (5). This project was an exploratory one, but recently much larger investigations have been initiated, including the California Aerosol Characterization Experiment (ACHEX) (Hidy et al. (6)), and a portion of the Regional Air Pollution Study (RAPS).

The key to improved characterization of photochemical aerosol behavior in the atmosphere is the quantitative description of the physical and chemical properties of this material as well as its kinetics of formation. A combination of observations, atmospheric simulation, and laboratory experiments is required to elucidate the complexities of particle evolution. The purpose of this paper is to review the current knowledge in these areas and to synthesize them into suggested key processes of interest in the atmosphere. First several important new results from the study of photochemical aerosols are outlined. Then conclusions from simulation experiments are related to recent basic investigations to elucidate relevant physico-chemical mechanisms applicable to the troposphere and the stratosphere. Finally a current picture of aerosol formation in the atmosphere is discussed in relation to the combination of evidence from field observations and knowledge of physical chemistry.

2. ATMOSPHERIC OBSERVATIONS

A. The Troposphere

Photochemical aerosols in the atmosphere require an operational or phenomenological definition. One definition might come from the comparison of the nature of suspended material from atmospheric samples and that generated in controlled laboratory experiments involving irradiated mixtures of reactive gases in air or filtered ambient air (e.g. Husar *et al*. (7)). In the atmosphere along, a definition becomes difficult because of the complexities of air chemistry involving a series of processes that are both sunlight induced and thermal in nature. A traditional operational definition of photochemical aerosols in the troposphere are those clouds of particles in air that are identified with hazes (a) where ozone is present, and (b) are formed and dissipated on a time scale of hours with maximum visibility degradation at mid-day. Perhaps the best known example is the intense haze formation associated with photochemical smog over the Los Angeles area. For the details of aerosol photochemistry one must rely heavily on observations taken in Los Angeles for they are far better documented than elsewhere.

One semi-quantitative measure of the concentration of haze is the extinction coefficient, b_{scat}, for visible radiation resulting from the scattering of light from airborne particles. Although b_{scat} has been found not to correlate uniquely with oxidant behavior, an important correspondence in the relationship appears to exist for b_{scat} taken when ozone is measured at its maximum on a given day in the Los angeles area. This relation is shown in Figure 1. Here the strong increase in light scattering (visibility reduction) with intensity of photochemical smog is demonstrated. The relationship is supported further by observations taken by blimp traveling at mid-day on a north-south path across zones of increasingly high ozone concentration over central Los Angeles.

Physical Properties

The scattering coefficient, b_{scat}, depends on the particle size-number distribution of the haze, the particle index of refraction as well as the wavelength of incident light. The number-size distribution and its moments can be considered the key physical properties of concern in characterizing atmospheric aerosol behavior. This distribution is often defined in terms of volume v, or the distribution function n (v,t,x) dv refers to the number of particles per unit volume in the particle volume range v and v + dv at any time t, and any point in space given by x. The particle size distribution is difficult to measure so that only moments of the distribution are monitored routinely. The zeroth moment of the distribution function corresponds to the total number concentration of particles, N, the two-thirds moment is proportional to the total surface area S per unit volume, and the first moment is proportional to the volume fraction, V. For particles of an average mass density $\bar{p}$, the product of $\bar{p}$ V is the total mass concentration; b_{scat} is a product of the Mie scattering function and S summed over all particle sizes. Evidence has accumulated from several experiments (e.g., Charlson _et al_.(8)), that b_{scat} is dominated by light scattering in the particle diameter range 0.1 μm to 1.0 μm. Indeed, observations taken in the ACHEX (6), as well as the 1969 Pasadena study show that particle evolution in smog is strongly concentrated in this size range. This is illustrated readily by measurements of the change in volume-diameter distribution from early to mid-morning in smog. An example of data taken in Pomona in 1973 is shown in Figure 2. These and other data also illustrate that few new nuclei smaller than 0.1 μm are produced in smog, in contrast to intense growth of existing particles during the evolution reactions of smog, which are believed to produce the condensable precursors.

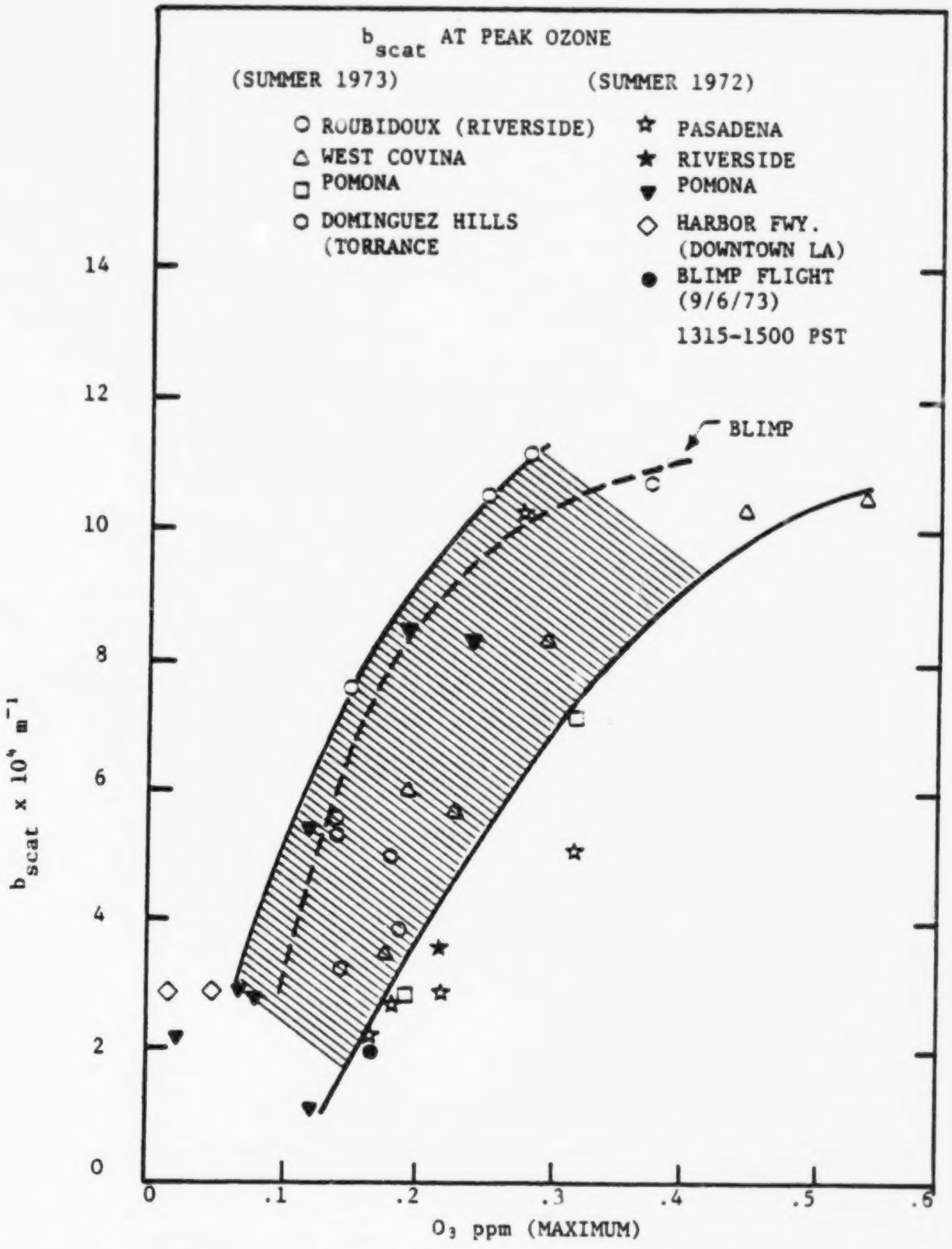

Figure 1. Correlation between b_{scat} and (O_3) max. Based on two hour averaged date taken in the Los Angeles Area (from Hidy *et al*. (6)).

Based on thermodynamic considerations Kelvin effect, there is reason to believe that the stability of aerosols is strongly influenced by the change in vapor pressure of materials with particle size. For most condensable species, the surface energies dictate that the stable particle is approximately 0.1 μm diameter, suppressing growth and new particle formation on ranges less than the size (see also Heisler et al.(9); Hidy (10)).

The fraction of particles smaller than 5-10 μm diameter is maintained at a low concentration by several removal processes including gravitational fallout (for details, see Hidy (11)). Haze evolution is most spectacular over cities with polluted air like Los Angeles because of high concentration of precursors combined with intense sunlight. However, it is believed that similar reactions must take place almost universally in the troposphere at slower rates, modulated by repeated irradiation by sunlight and intermittent removal processes involving clouds.

Chemical Properties. Chemical analysis of airborne particles provides the most revealing information about the nature and significance of aerosol formation by atmospheric chemical processes. There is an accumulation of information from many studies, as reviewed, for example, by Junge (12) and from more recent reports such as those of the National Air Surveillance Network (13), that water soluble sulfate, nitrate and organics make a substantial fraction of the tropospheric aerosol. The importance of these constituents is illustrated in Table 1 for urban and non-urban aerosol samples in California. Examination of such samples also suggests that the sulfate and nitrate exist as ammonium salts through observations in other geographical areas may indicate the presence of sulfuric acid For example, Charlson et al. (14) have reported evidence of free sulfuric acid from non-urban air near St. Louis, and Cunningham (15) has identified by infrared analysis sulfuric acid in urban samples of aerosol collected near Chicago.

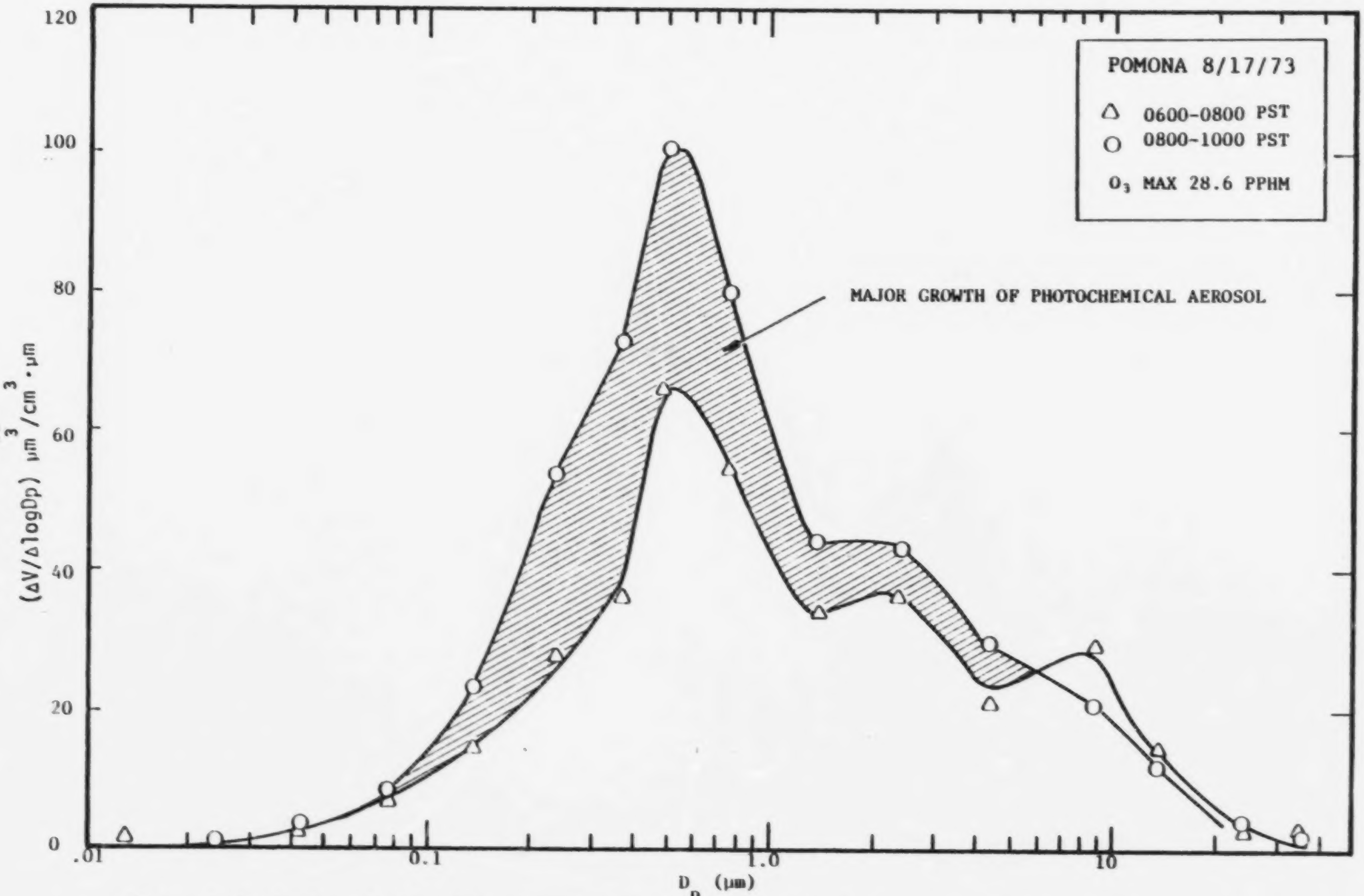

Figure 2. Evolution of the volume distribution of smog aerosol taken at Pomona, California 8/17/73 (from Hidy et al. (6)).

Table 1

Chemical Composition of Filter Collected Aerosol Samples

	Weight Percent			
	Non-Urban		Urban	
Constituent	Pacific Coast* Offshore	Desert⁺	Fresno⁺	Pomona⁺
Al	2.8	2.4	2.4	0.99
Si	5.0	5.2	6.3	2.2
Na	3.6	0.71	0.40	1.1
Cl	9.9	0.32	0.19	0.51
K	1.3	0.39	0.33	0.24
Ca	1.9	2.1	0.47	1.0
Ti	0.15	0.13	0.09	0.11
V	N.D.	0.004	N.D.	0.008
Cr	0.02	N.D.	0.0058	0.013
Mn	0.04	0.028	0.025	0.025
Fe	1.6	1.4	1.03	0.86
Cu	0.6	0.028	0.0058	0.014
Zn	0.2	0.035	0.055	0.13
Br	0.2	0.059	0.098	0.36
PB	0.4	0.017	0.42	1.6
I	-	-	-	-
$SO_4^=$	17.5	2.8	2.0	10.6
NO_3^-	5.7	3.5	3.8	20.2
NH_4^+	2.2	1.7	1.5	9.1
Non Carb. C	3.0	N.D.**	5.0⁺⁺	24.0⁺⁺
Total measured ($\mu g/m^3$)	30	42.4	207	180

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*Average of 20 samples at San Nicolas Island (Hidy *et al*. (64))

⁺Single 24 hour sample (Hidy *et al*. (6))

⁺⁺Estimated as 3 x cyclohexane extractable organics

**Not detected

The mass concentration of sulfate and nitrate cannot be accounted for from either natural or man made primary sources (Robinson and Robbins (16); Hidy and Brock (17)). Thus the production of aerosols in the atmosphere is believed to involve mainly the highly complex chemistry of sulfur, nitrogen, and organic carbon. These constituents come from gaseous emissions of both natural and anthropogenic origin and are key ingredients in the "classical" hierarchy of gas reactions in photochemical smog. Most of the nitrate appears to be inorganic, with only a minor organonitrate contribution, evidently linked with photo-chemical processes (O'Brien et al.(18) and Hidy (10)).

The organic fraction is characterized by more oxygenated material than accounted for in the vapor. High resolution mass spectroscopy and solvent extraction methods, combined with infrared analysis, suggest that more than half the organic aerosol os oxygenated, with a large carboxylic acid component (e.g., Schuetzle (19); Hidy et al.(6); and Grosjean and Friedlander (20)).

The size distribution of "secondary" aerosol constituents is of interest for checking the evolutionary processes indicated by physical measurements. Observations of the mass concentration of sulfate over two hour intervals in smoggy air over Los Angeles and other cities indicates that at least half of this material is found in the fraction of aerosol less than 1.0 μm diameter. Under conditions of heavy smog, most of the sulfate in Los Angeles air is concentrated in the small particle fraction during the day, but at night and in the early morning the sulfate shifts to larger particles (Hidy, et al. (6)). In contrast, nitrate appears to be present in somewhat larger particles in the Los Angeles aerosol except in areas such as Riverside which is far downwind of the city under the most common daytime conditions.

The distinction between the size distribution of sulfate and nitrate in smog aerosol is illustrated in the data shown in Figure 3. The case shown in Figure 3A corresponds to a 24 hour sample in West Covina, California during which the maximum ozone concentration exceeded 0.4 ppm in the east central part of the Los Angeles Basin. Another case from the Riverside area farther east is shown in Figure 3B in which the maximum ozone concentration was above 0.3 ppm. These samples illustrate that the mass distribution of nitrate and sulfate constituents in more aged smog than that at West Covina is almost identical, but much more nitrate is present downwind, farther to the east.

Diurnal Patterns of Evolution. An important description of the evolution of photochemical smog comes from examination of the changes during the day of the reactive gases in the air. The classical picture of smog formation is revealed in the set of data in Figure 4. Here the familiar pattern of early morning depletion in NO and hydrocarbons takes place with a mid-morning maximum in NO_2 and a mid-day maximum in ozone concentration. Such behavior has been simulated successfully many times in smog chamber experiments. Accompanying the increase in ozone is the increase in b_{scat}, reflecting the aerosol growth and subsequent visibility reduction in smog through the mid-day. Changes in total number concentration are less well correlated with the reactives gas behavior, and are more closely related to local combustion sources.

The diurnal changes in sulfate, nitrate, and carbon constituents accompanying the gas chemistry are shown in Figure 5. In many (but not all) cases studied in ACHEX (Hidy et al.(6)), observations showed that sulfate and non-carbonate carbon follow closely the ozone development with maxima in mid-afternoon. $SO_4^=$

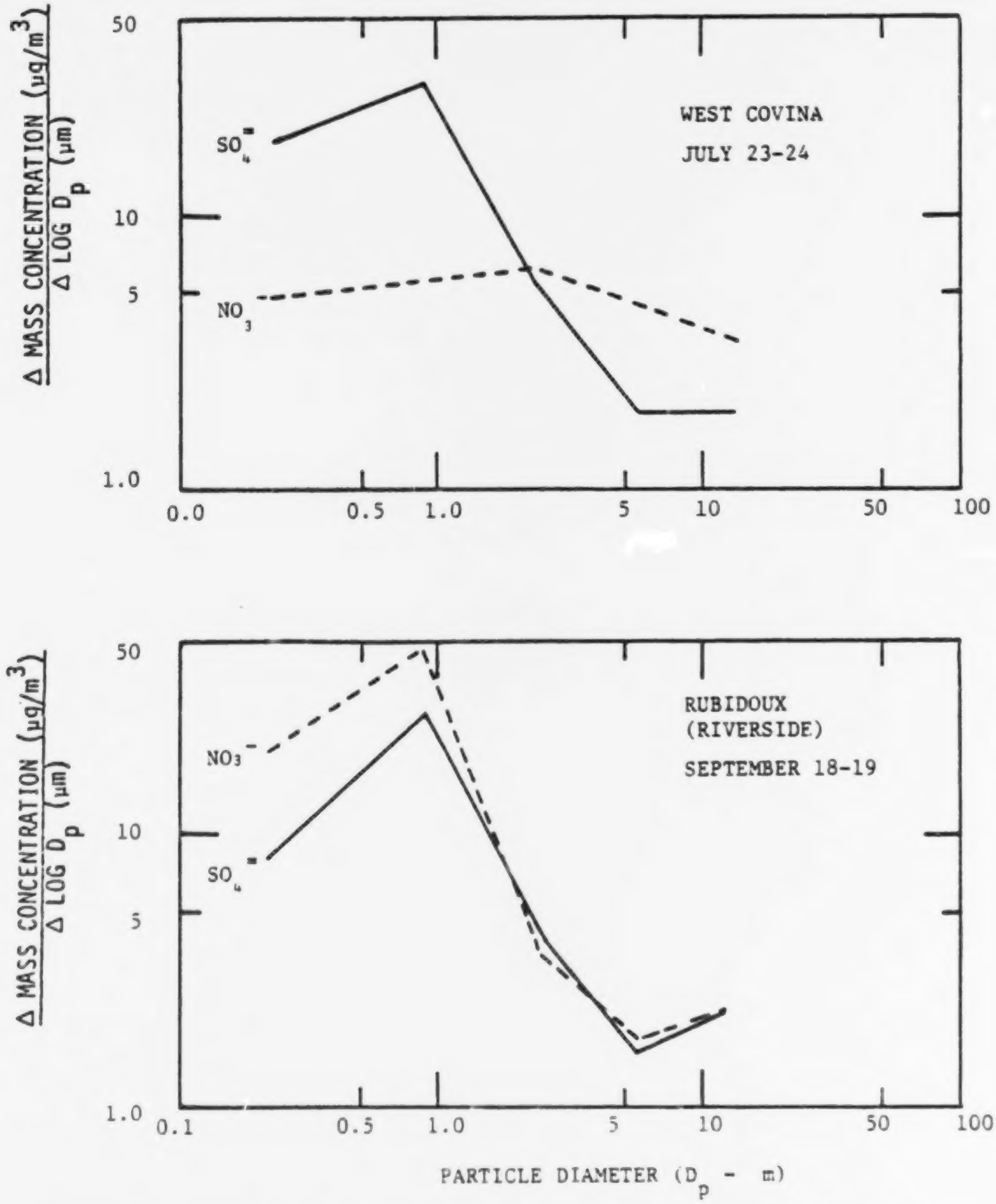

Figure 3. Mass Distributions of $SO_2^=$ and NO_3^- With Particle Size at two Locations in Los Angeles (Data from Hidy et al. (6)).

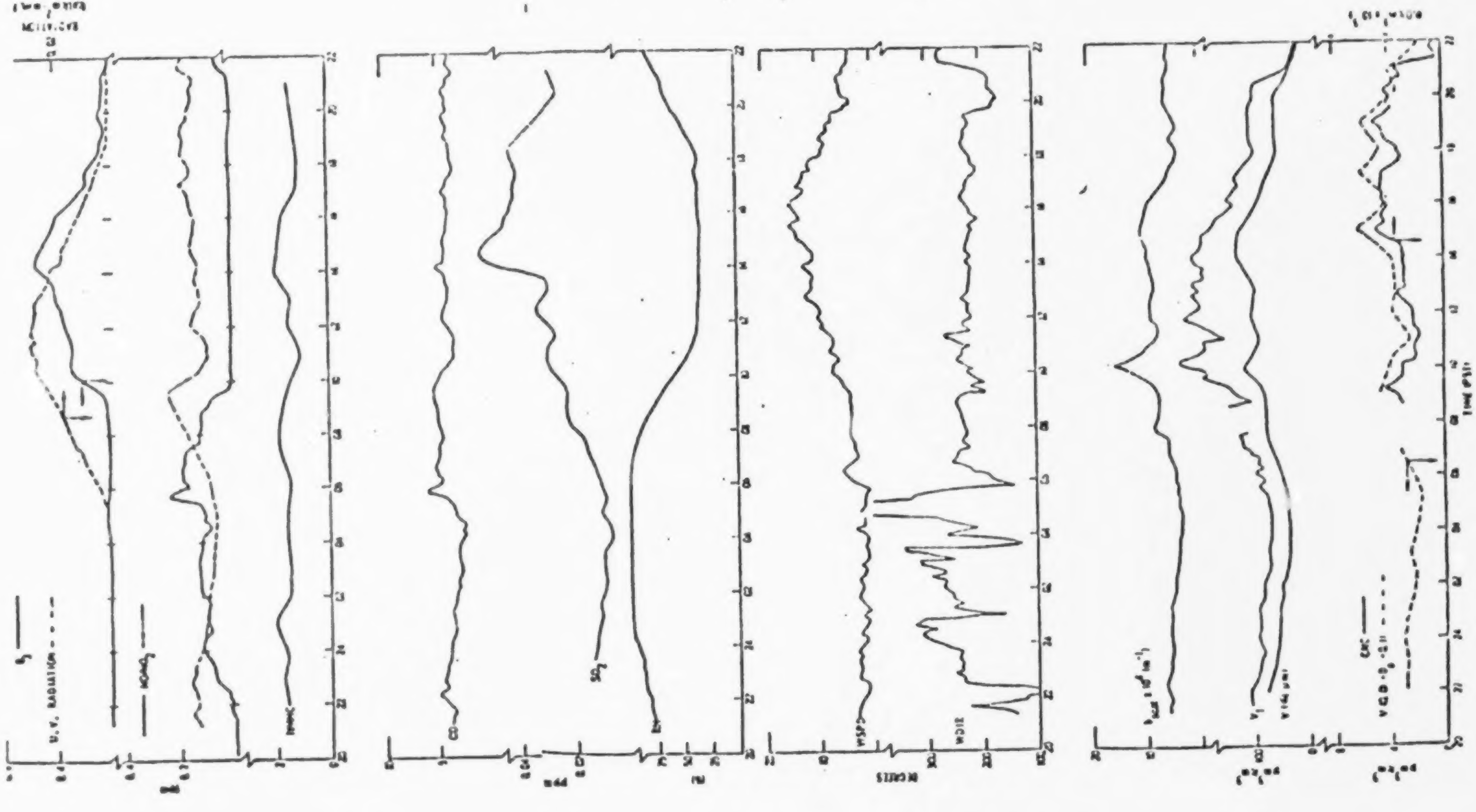

Figure 4. Diurnal patterns for West Covina, July 23-24, 1974. V_T - total particle volume, V(< 1 μm) - particle volume less than 1 μm diameter, V(0.01 > Dp > 0.1) - particle volume in the range 0.01 - 0.1 μm diameter (Dp), and CNC - condensation nuclei count (from Hidy et al. (6)).

also follows SO_2 changes during the day. In contrast, nitrate was found to develop a maximum concentration by mid-morning with the NO_2 pattern. Thus the components of the aerosol behave in different ways, and evidently sulfate and organics are generated by distinctly different chemical mechanisms from nitrate.

Conversion Ratios. A useful measure of the extent of conversion of an aerosol precursor with condensed material is the so-called conversion ratio as follows:*

$$f_S = \frac{\text{mass of particulate sulfur based on } SO_4^{=}}{\text{mass of particulate sulfur + mass of gaseous sulfur based on } SO_2}$$

$$f_N = \frac{\text{mass of particulate nitrogen based on } NO_3^{-}}{\text{mass of particulate N + mass of gaseous N based on } NO_2}$$

$$^{*}f_C = \frac{\text{mass of particulate non-carbonate C - primary non-carbonate C}}{\begin{array}{l}\text{mass of particulate non-carb. C - primary non-carb. C + mass of} \\ \text{reactive gaseous C from NMHC}\end{array}}$$

In the troposphere, the data on these ratios are limited, but a few values are given in Table 2 for comparison. Depending on the location

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*The secondary organic carbon is defined as the total non-carbonate carbon less the carbon identified with motor vehicle sources. For Los Angeles, the latter is accounted for approximately as a factor α proportional to the airborne lead concentration. α is taken as unity for the purposes of this study, after Friedlander (62). NMHC = non methane hydrocarbon vapor concentration in $\mu g/m^3$.

Table 2

Some Examples of Conversion Ratios from Atmospheric Observations

(Numbers in parentheses are heights above the ground)

Investigator	Location	(%)		
		f_S	f_N	f_C
Georgii (63)	Colorado	19 (5 km)	-	-
	Germany	17 (0.8 km)	-	-
		77 (2.8 km)	-	-
Rhode (67)	Sweden	6.7-14.3(0.4-2.8 km)	-	-
Cuong, et al (66)	Antarctic	90	-	-
	South Pacific	86	-	-
	Mediterranean	72	-	-
Grosjean & Friedlander (20)	Pasadena	29	5.8	3.3*
ACHEX (6)	East/Central Los Angeles Basin	21	6.6	0.44
	Eastern Los Angeles Basin	27	31	0.60

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*defined without correction for primary C contribution.

of sampling, the values of the conversion ratios vary widely, but air masses containing aged aerosol or intense photochemical smog conditions appear to give the highest values.

The diurnal changes in f_S and f_N corresponding the behavior of the reactants and products in West Covina are shown in Fig. 5. Typically, f_S remains roughly constant during the day with a value of approximately 0.2 while f_N is more variable with a maximum in the night through mid-morning in this case. In the Los Angeles area, $f_N \approx 0.06$ in central areas, while it reaches more than 0.30 farther downwind in Riverside.

The conversion ratio for carbon, f_C, is indicated according to the definition above in Fig. 5. In this case, it displays a maximum in mid-afternoon accompanying the ozone peak, with average values equal to or less than 0.01.

The conversion ratio f_C can be defined in a somewhat better way without assuming arbitrarily that the organic aerosol precursors are uniquely proportional to the non-methane hydrocarbon concentration. In some cases, the NMHC concentration has been measured through C_6 with chromatographic analysis (6). In view of certain later discussion, a better normalization for f_C might be in terms of the mass of non-carbonate carbon plus the mass of total NMHC minus the NMHC $\leq C_6$, f_{C6}. Using this definition, f_{C6} is the same for f_C, but the former ratio is somewhat smaller because of the conversion factor from ppm HC to $\mu gC/m^3$ used.*

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*For f_C, NMHC are determined using NMHC as propane, or the gas density is 2×10^{-3} gm/cm^3. For hydrocarbons and vapors $\leq C_6$, a vapor density of 4×10^{-3} gm/cm^3 has been assigned for purposes of the calculation.

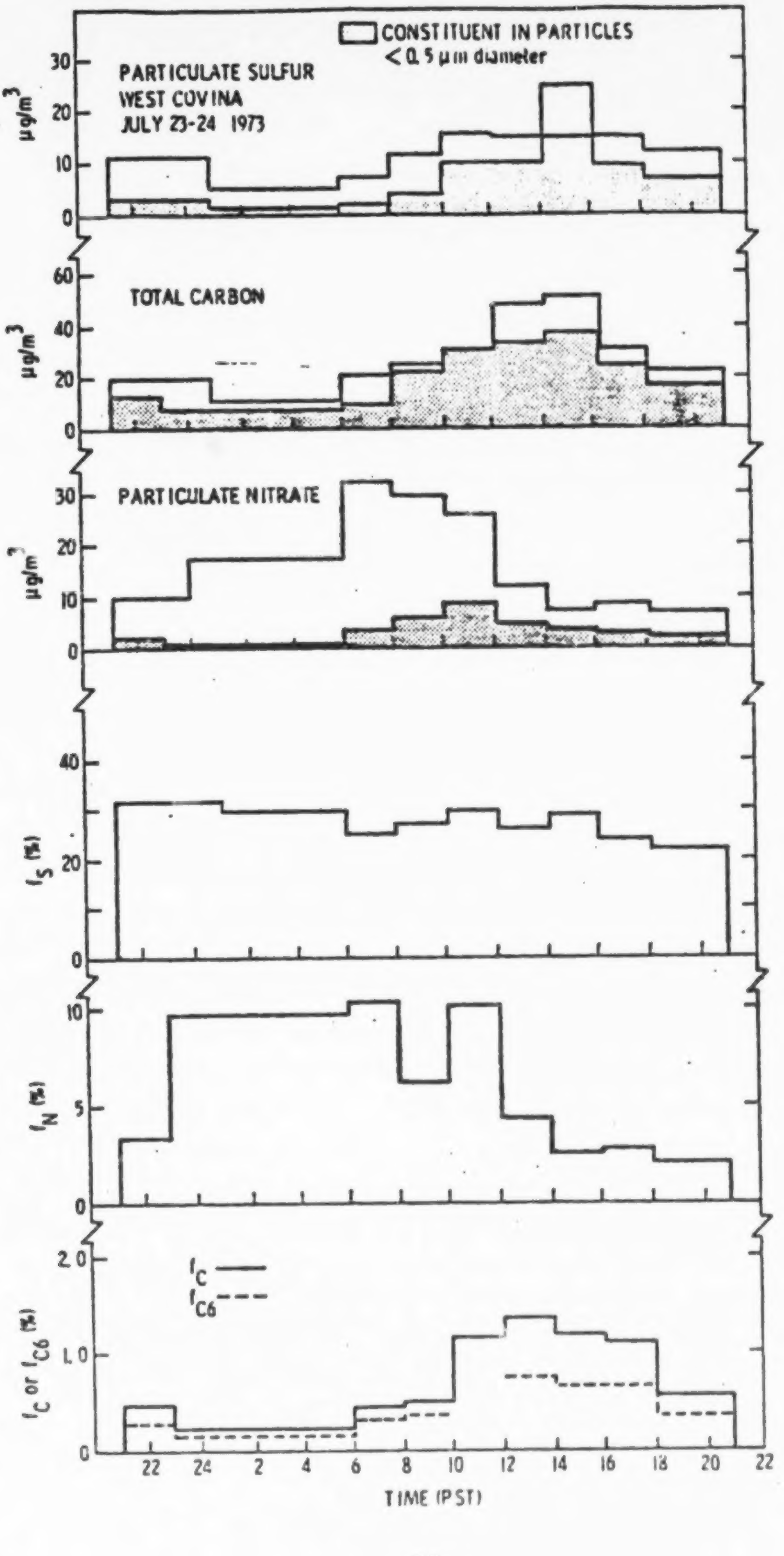

Figure 5. Aerosol Diurnal Pattern for West Covina, July 23-24, 1974 (Data from Hidy *et al.* (6)).

Comparison between f_S and f_N between West Covina and Rubidoux (Riverside) much farther eastward (downwind) of the Los Angeles area shows that f_S is roughly the same in both locations. Yet f_N was found to be significantly higher at the downwind site. Thus qualitatively, the sulfate production process appears to generate a relatively uniform conversion over Los Angeles even though the principal sources of SO_2 are on the West and Southwest portion of the Basin. In contrast, there appears to be two distinct modes of nitrate production, one a rapid, localized process peaking with morning NO_x or NO_2, and one that is more slow, causing daily accumulation of NO_3^- far downwind of major NO_x sources in Los Angeles.

Comparison of the variation in conversion ratios with key changes in trace gases provides additional insight into the mechanisms of aerosol formation in the atmosphere. For example, analysis of the ACHEX data taken in 1973 shows that f_S is not significantly dependent on relative humidity. But f_S for particles less than 0.5 μm diameter is negatively correlated with relative humidity. Furthermore, a strong apparent influence of photochemistry is demonstrated for submicron sulfate formation by the systematic increase in f_S ($\leq$ 0.5 μm) with ozone concentration. The consistency of this trend is shown in Fig. 6.

Further clues of the sulfate formation mechanism come from comparison of sulfate conversion and the behavior of particulate non-carbonate carbon. The conversion ratio f_S ($\leq$ 0.5 μm) is correlated with changes in particulate carbon, as indicated in Fig. 7. Thus the formation of aerosols involving sulfate and organic carbon are closely coupled in Los Angeles smog.

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*For f_C, NMHC are determined using NMHC as propane, or the gas density is 2×10^{-3} gm/cm^3. For hydrocarbons and vapors $\leq C_6$, a vapor density of 4×10^{-3} gm/cm^3 has been assigned for purposes of the calculation.

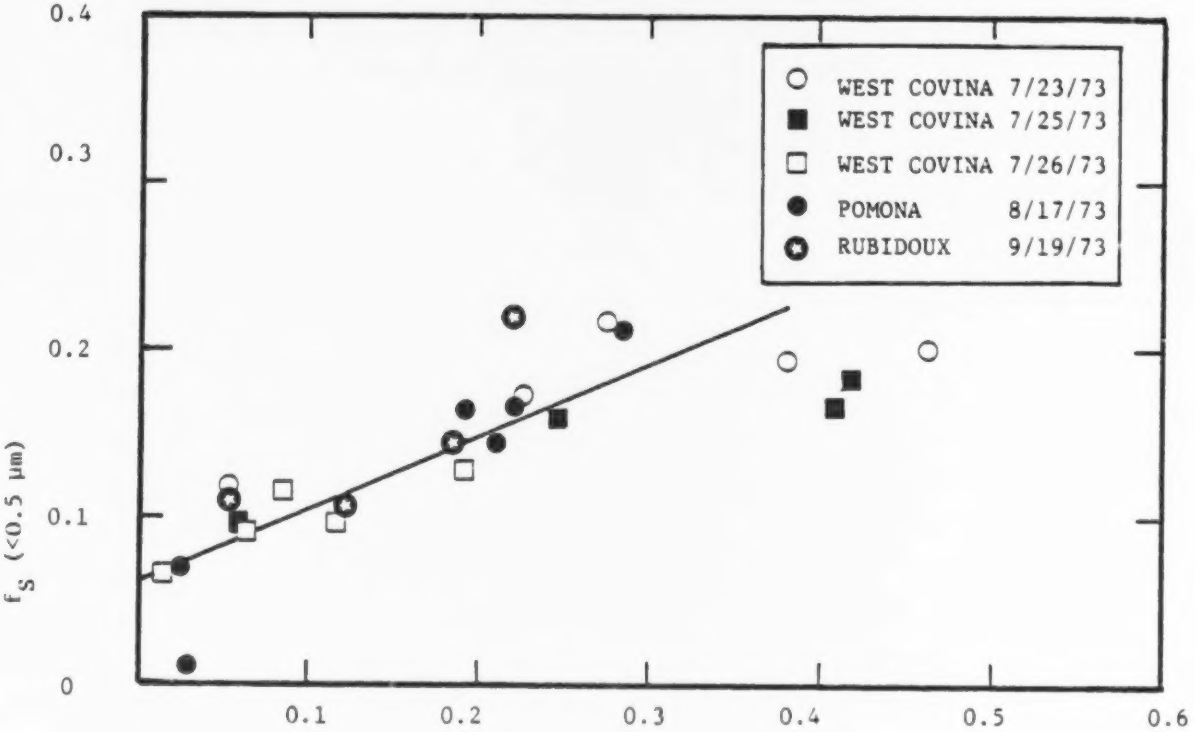

Figure 6. Scatter diagram of the conversion ratio f_S based on particles less than 0.5 μm vs. 2 hour averaged ozone concentration (data from Hidy et al. (6)).

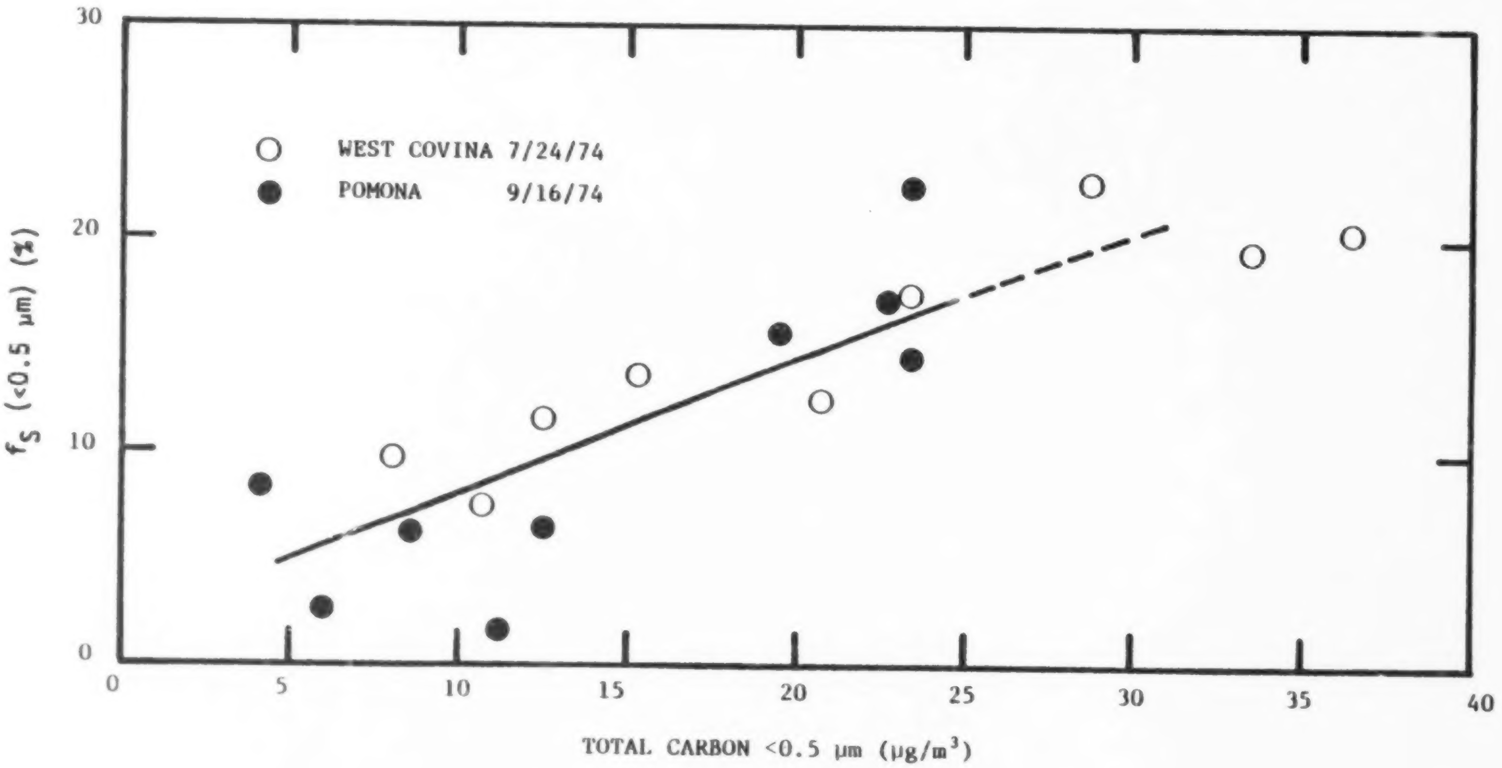

Figure 7. Scatter diagram of the conversion ratio f_S based on particles less than 0.5 µm vs. total carbon less than 0.5 µm diameter. (Based on 2 hour averaged filter data.) (Data from Hidy et al. (6)).

The behavior of particulate nitrate is difficult to explain phenomenologically. It is puzzling, for example, that f_N for either the total particle mass concentration or that confined to 0.5 μm is poorly correlated with humidity as well as NO_2, NO_x, and ozone concentration. The apparent independence of f_N or NO_2 is illustrated by the scatter diagram shown in Fig. 8. Such results suggest that high nitrate content of the aerosol cannot be the result of a spurious absorption of gaseous NO_2 at the moist filter medium. For if this were the case, one would expect a proportionality between f_N and NO_2 concentration. By the same arguement, NO_3^- does not appear to form by a gas diffusion limited absorption of NO_2 in wet particles. On the other hand, the data suggest that the conversion process to nitrate may be dominated by other nitrogen oxide intermediates such as NO_3^-, N_2O_5, or HNO_3 which build up in the morning with the photochemical activity. However, these intermediates are more likely to be in high concentration at mid-day rather than mid-morning in smog. The rapid transient increase in nitrate in the mid-morning does not seem to be related closely to the systematic increase in nitrate eastward across the Los Angeles Basin.

Estimated Rates of Conversion. The information presently available is very limited on the rates of conversion of aerosol precursor gases in the atmosphere. There are reports in the literature that tropospheric residence times of SO_2 and NO_x are the order of a few days, while reactive hydrocarbon vapors of high molecular weight evidently will not survive more than a day.

Some estimates of the quasi-first order rates of SO_2 oxidation have been reported that range from 0.1% to ∿ 10% hour^{-1} depending on many factors, including relative humidity (e.g. Calvert (21)). Recent work, for example, of Husar et al.(22) near St. Louis suggests an oxidation rate of less than 1% in the absence of photochemical reactions. However, in the presence of photochemical activity SO_2 oxidation rates varying from 2 to 13% hr^{-1} have been estimated from Los Angeles data by Roberts and Friedlander (23).

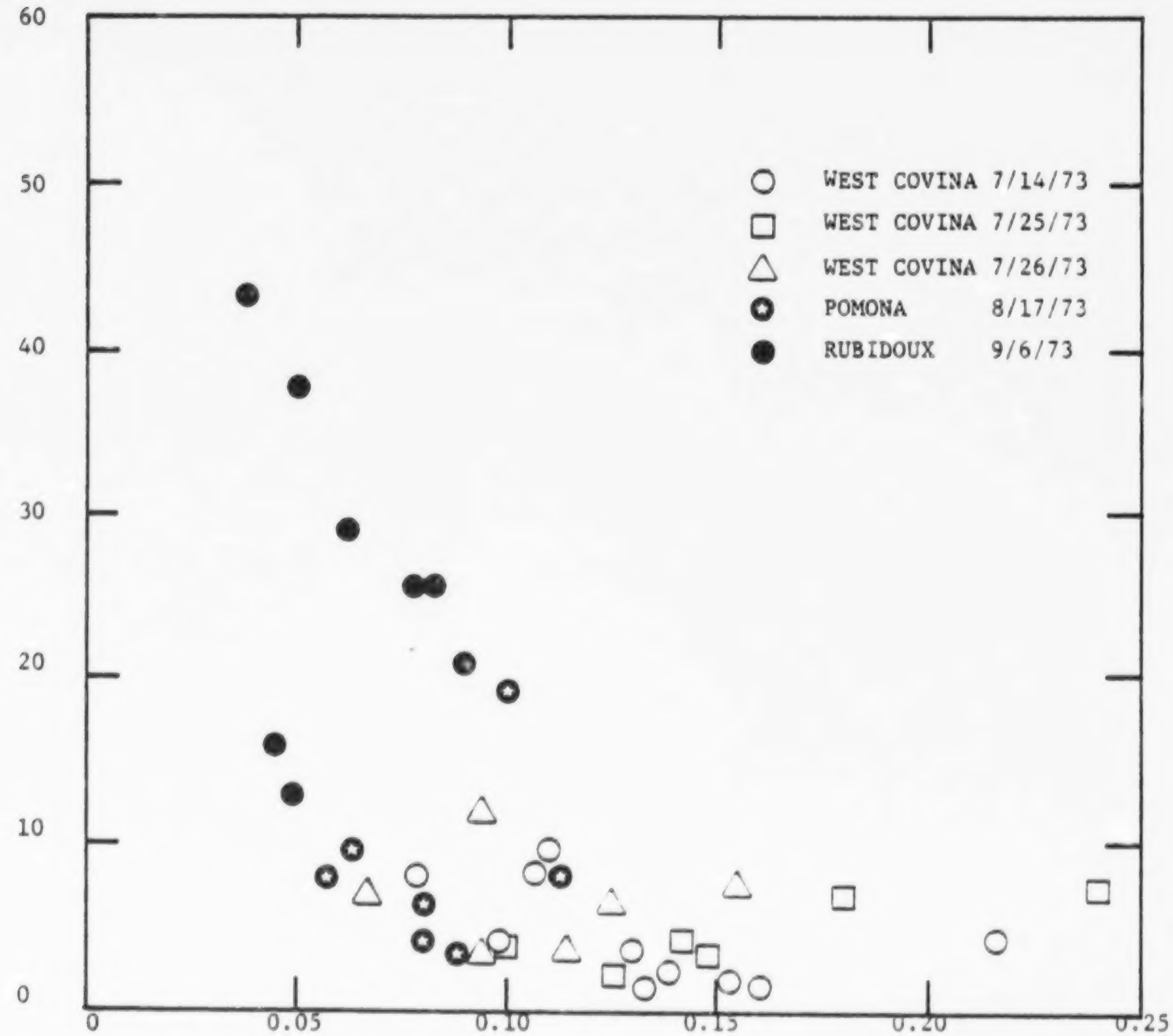

Figure 8. Scatter diagram of the nitrogen oxide ratio f_N vs. two hour NO_2 concentration (data from Hidy et al. (6).

Crude calculations based on data from the ACHEX (6) indicate similar rates of oxidation of SO_2 in the Los Angeles Basin.

There is virtually no quantitative information on the conversion rates of NO_x to nitrate available. However, the Los Angeles experience previously discussed suggests that two extremes may be present. A rapid transient conversion may exist as a part of the morning photochemical nitrogen oxide cycle, giving a formation at high humidity of some nitrate at a local production rate exeeeding SO_2 oxidation. In contrast, there appears to be a second nitrate forming process that may be similar to the sulfate conversion rate, or slower depending on the location of the principal sources of NO_x. This conclusion comes from the marked differences downwind in nitrate and sulfate distribution in the Los Angeles Basin.

The rate of organic aerosol production in the troposphere is essentially unknown. On the basis of the Los Angeles data, however, the conversion rate should be about the same as the sulfate formation rate because of the close diurnal correspondence between the two. The conversion rate of certain hydrocarbons may be even faster than sulfate since the hydrocarbon vapor sources are more evenly distributed over the city than the sulfur oxide sources. Yet the conversion ratio for organics as presently defined is substantially less than that for sulfate or nitrate.

Summary

The existing knowledge of the phenomenology of aerosol formation in the troposphere relies heavily on the photochemical smog observations in Los Angeles. A summarizing list of key observations is given in Table 3.

Table 3

Some Properties of Tropospheric Aerosols Relevant to Their Formation Chemistry

Phenemenon	Urban	Non-Urban
1- Production of new particles	limited	limited
2- Formation of nuclei in filtered, irradiated air	copious nuclei generated	uncertain
3- Haze formation & optical scattering	strong diurnal changes accompany smog evolution (Los Angeles); correlation of scattering with maximum daily ozone	widespread regional increase of haze over continents below 3-5 km altitude
4- Particle growth in 0.1-1.0 m diameter range	predominant	predominant
5- Role of liquid water in particle growth	strong evidence supporting role in growth - urban aerosols generally hygroscopic	suspected; not proven universally
6- Key Chemical Components		
...Carbon-oxygenated organics	major constituent, sometimes produced by reactions; confined to submicron particles	highly variable constituent, but normally present
...Sulfate	universally present; large fraction in submicron range; submicron particle production depends on ozone; production correlated with organics; not correlated with humidity	universally present
...Nitrate	universally present; highest concentration in photochemical smog or in high humidity with NO_2 (not correlated with NO_2 or $SO_4^=$ concentration); sometimes in larger particles than sulfate; spatial distribution in Los Angeles differs from sulfate	normally present

Table 3 (continued)

Phenomenon	Urban	Non-Urban
...Ammonium	normally present; often insufficient to "neutralize" acid anions	normally present; usually insufficient to "neutralize" acid anions
7- Conversion Ratios		
f_S sulfate sulfur to total sulfur	~ 0.1 (within hours of SO_2 source); observed 2 hr. average maximum ~ 0.6 in aged air without new sources of SO_2 rate of formation 1%-15% hr^{-1}	sometimes approaches unit in upper troposphere
f_N Inorganic nitrate to total oxidized nitrogen	~ 0.1 (hours from sources); observed 2 hr. averaged maximum ~ 0.4 in smog	uncertain
f_C organic carbon to carbon in non-methane hydrocarbons	0.005-0.020 (based on non-methane hydrocarbons) in Los Angeles	unknown

B. The Stratosphere

The principal evidence for aerosol formation in the stratosphere comes from the discovery in the early 60's and the subsequent confirmation of the dominance of sulfate in aerosols samples taken at high altitude. Observations have suggested the presence of a maximum concentration of particles greater than ~ 0.1 μm diameter at altitudes of about 20 km. The "model" composition for the stratosphere aerosol is shown in Table 4. These data, based on the work of several investigators including Junge et al.(24) and Lazrus et al.(25), show that sulfate is by far the major component of aerosol at altitudes of ~ 20 km.

In contrast to the tropospheric material, both nitrate and organics, as presently reported, are essentially absent from the stratospheric particles. In the latter case, this is not surprising because it is expected that condensable organic vapors would have to be high in molecular weight and probably would not survive substantial degradation above the tropopause. The absence of nitrate in the aerosol evidently is related to the high vapor pressure of HNO_3 relative to H_2SO_4 (see below); NH_4^+ or cations other than N^+ in large quantities are not expected to be present at high altitude. Apparently, the most acceptable steady-stage theory for the presence and profile of sulfate comes from (photochemically related) oxidation of SO_2 in situ at high altitude (e.g., Friend et al.(3), Junge (26), Harrison and Larson (27)).

The details of the physical mechanism of sulfur oxide transition into particles are unknown in the stratosphere. The evidence from size distribution observations combined with nuclei and optical data suggests, however, that stable sulfate accumulation takes place mainly in existing particles rather than through formation of new nuclei. There is a general depletion in nuclei concentration with altitude, but the particle number in the range ~ 0.1 μm diameter varies a much smaller amount with height (e.g., Hidy et al. (28)).

Table 4

Model Chemical Composition of Stratospheric Particles at 20 km Altitude During the Period 1969-1973. Source: Hidy et al. (28).

Substance	Concentration in air $\mu g/m^3$ (ambient)	Observed concentration range $\mu g/m^3$ (ambient)
Sulfate	0.6[c]	0.01 - 4 (Agung peak)[c]
Basalt[a] (calculated from Si)	0.05	0 - 0.7
NH_4^+	0.005	0 - 0.01
NO_3^- [b]	0	0
NO_2^-	0	0
Na	0.01	0.001 - 0.05
Cl	0.04	0.002 - 0.09
Br	0.002	0 - 0.003
Total	0.71	0.01 - 1

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[a] This includes all other components of the basalt, e.g., Al, Ca, Mg.

[b] Particulate NO_3^- as contrasted with HNO_3 vapor.

[c] For eight-year averaged data at 18 km from Castelman _et_ _al_. (65).

Based on the few existing measurements, the number mean diameter for stratospheric aerosols is approximately 0.5 μm, and the total mass concentration is estimated to be 0.1-1.0 μg/m^3 at 20 km.

The rate of oxidation of SO_2 above the tropopause is unknown and very difficult to estimate because no data on SO_2 concentrations above 10 km are available. Rough estimates of the reaction time for SO_2 based on known SO_2 oxidation chemistry now range from months (Harker (29)) to many years (Friend et al. (3)). The former is accepted by most chemists as the more likely value.

3. MECHANISMS FOR AEROSOL FORMATION

The chemical and physical processes that lead to aerosol formation in the atmosphere are probably very complex, with no single mechanism dominating the phenomenon. Unlike the chemical laboratory, the atmosphere is very "dirty" in that it contains substantial amounts of airborne particles which are continuously interacting with trace gases. Water as vapor and in the condensed phase likely plays a critical role in aerosol evolution, both in growth and removal from the atmosphere. Thus, in elucidating atmospheric aerosol behavior, one must account for both homogeneous processes of precursor formation and heterogeneous interactions.

A. Physical Constraints.

Regardless of the chemistry, certain physical constraints exist on aerosol-gas interactions. These restrictions relate mainly to (a) the thermodynamic stability of condensed particles of small diameter, (b) particle nucleation and condensation processes, and (c) gas phase diffusion limited rates combined with absorption or adsorption on particles.

Particles must be close to or at equilibrium with respect to the surrounding vapor to exist in air for any length of time. Thus, the partial pressure of condensed species on particles essentially must be less than or equal the saturation vapor pressure at atmospheric temperature for stability. This presents no great problem for most inorganic salts or for sulfuric acid, even at parts per billion concentration in the gas phase. However, it places a severe constraint on the ability of HNO_3 to exist as a pure compound or as an acid diluted in water.* The vapor pressure data reviewed by Toon and Pollack (30), for example, indicates that HNO_3 has a partial pressure over aqueous solutions more than 100 times higher than concentrated H_2SO_4 making nitric acid far less stable in the atmosphere than sulfuric acid.

The requirements of low vapor pressure are particularly important to the stability of organic aerosols. The bulk of the organic vapors in the atmosphere that have been identified are in range of carbon number less than four. Even if such materials reacted to form oxygenated materials, review of vapor pressure data (Hidy (10)) suggests that only material of carbon number much greater than C_6 would be thermodynamically stable in the condensed phase at the concentrations of $\sim$ 1 ppb.

Accumulation of condensed material as aerosols in the atmosphere may take place by two basic processes: first by condensation of super-saturated vapor or by chemical reaction leading to spontaneous formation of new particles; second, by condensation, absorption or reaction on existing particles. In the latter case, the chemical reactions actually may take place on the surface of, or within existing particles.

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* Vapor pressure data for HNO_2 or HNO_3 over solutions of ammonium sulfate or sulfuric acid are not readily available so that the volatility of these acids over multicomponent aqueous media is unknown.

For condensable precursors, the rate of particle formation may occur by homogeneous nucleation or by hetrogeneous nucleation. It is generally accepted, but not proven, that heterogeneous processes are most likely in the atmosphere because of the large number of existing nuclei. One can readily see, however, that growth by condensation is limited by the rate of diffusion of vapor to the surfaces of nuclei. If conditions exist in which aerosol precursors evolve chemically at a rate exceeding the diffusional transfer, then supersaturation could build up to high enough levels to permit heteromolecular (homogeneous) nucleation of new particles. It can be shown that H_2SO_4 can undergo heteromolecular nucleation at atmospheric concentrations in the absence of nuclei, but it is unlikely that HNO_3 could nucleate because of its relatively high vapor pressure. So little is known about the products of aerosol forming organic reactions and their relevant physical properties that nothing can be said about the importance of homogeneous nucleation in this case.

The fact that few new particles are observed in cities away from combustion sources or in rural areas, particularly in highly reactive atmospheres like Los Angeles make it unlikely that heteromolecular nucleation is a widely important formation process in the troposphere. The general decrease in nuclei concentration with altitude with more nearly constant large particle concentration suggests that new particle formation normally plays a small role at high altitude, too. Yet, this conclusion is by no means well established in the case of sulfuric acid behavior above 10 km altitude.

Growth of particles by accumulation on existing particles can be classed as two broad processes. If the precursor is supersaturated, growth will occur at a vapor diffusion limited rate, which depends on the supersaturation, the temperature, the particle size, and the accommodation coefficient at the surface. The proportionality of particle size changes with the ratio of particle diameter and mean free path of the suspending gas. At one extreme, the growth depends on volume to the 2/3 power; at the other, growth is proportional to volume to the 1/3 power. When the precursor is unsaturated, growth still may take place by irreversible absorption, or by chemical reactions in the particle. In this case, the rate law should be proportional to the particle volume if the reaction is uniform throughout the particle. If the formation of material is limited by reactions in the particle, then the conversion ratio should not be dependent on the gaseous precursor concentration.

There is insufficient data available to determine the rate law or physical mechanism most likely to predominate in atmospheric aerosol growth. However, there are clues to differences in the processes from the Los Angeles data. The shape of the particle volume number distribution of tropospheric aerosol is such that the 1/3 (diameter) and 2/3 (surface) moments are concentrated in the submicron fraction, while the first moment (volume) is weighted toward larger particles. Thus the observed accumulation of sulfate and organic carbon on the small particles in smog suggests a surface or vapor diffusion controlled process. In contrast, the collection of NO_3^- in larger particles and independence of NO_2 may indicate a volume controlled reaction in particles. The shift in NO_3^- to smaller particles between the east central and the eastern parts of the Los Angeles Basin is of interest in this case and remains unexplained.

It is of interest that the influence of thermodynamic equilibrium must enter the growth process of particles. If the radius of the particles is too small, the partial pressure condensable species can increase significantly by the influence of radius of curvature. From Kelvin's relation, examination of values of surface tension for a range of materials suggests that this effect will constrain growth to particles greater than 0.05 - 0.1 μm diameter. This appears to be consistent with available observations of atmospheric growth and the distribution of secondary chemical components.

B. Chemical Reactions for Precursors.

Physical processes of phase change, absorption and stabilization restrict the maximum rate of formation and the classes of materials expected in aerosols generated in the atmosphere. Yet in many instances, the rate controlling process in the production mechanism may be the precursor formation. In the case of any of the three secondary constituents, there are a variety of possible chemical mechanisms that may occur in the atmosphere. It is likely, in fact, that different mechanisms take place in parallel, or complement one another so that no one process is the dominant one. One example of this is the difference in behavior of sulfate in Los Angeles air, as indicated by the changes in sulfate-particle size distributions.

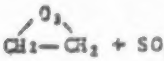
Sulfate Reactions

The oxidation reactions of SO_2 have been reviewed by several investigators including Bufalini (31) and Calvert (21). There are more than a dozen sulfate forming reactions that may be relevant to atmospheric processes. These can be grouped in terms of homogeneous gas phase reactions and heterogeneous reactions involving suspended particles. A summary of the two groups is listed in Tables 5 and 6. The homogeneous reactions are broken down into subcategories whose end products are SO_3 or RO_2SO_2, and $ROSO_2$. Although the rates of reaction of these species with water or other species have not been reported, it is assumed that the reactions with water are fast to form H_2SO_4 and not the rate determining step in $SO_4^{=}$ production.

Listed in Table 5 are three classes of homogeneous reactions. The first consists of inorganic oxidation mechanisms to form SO_3, while the second involves organic radical oxidation agents generating SO_3 or RO_2SO_2. The third group of reactions forms $ROSO_2$ species. All of the reactions listed are exothermic and are favored thermodynamically. However, the first five reactions have been considered severely rate-limited on the basis of available rate data (e.g. Calvert (21)). The remaining reactions listed appear to have rates

Table 5

Estimated Rates of Theoretically Possible Homogeneous Removal Paths for SO_2 in a Simulated Polluted Atmosphere (from Calvert (21))

	ΔH_{298° kcal/mole	Approx. Rate, % per hr.
A. Inorganic Reactions Forming SO_3		
(1) $SO_2 + 1/2\ O_2 + \text{Sunlight} \rightarrow SO_3$	−24	< 0.021
(2) $O(^3P) + SO_2 + \underline{M} \rightarrow SO_3 + \underline{M}$	−83	0.014
(3) $O_3 + SO_2 \rightarrow SO_3 + O_2$	−58	0.00
(4) $NO_2 + SO_2 \rightarrow SO_3 + NO$	−10	0.00
(5) $NO_3 + SO_2 \rightarrow SO_3 + NO_2$	−33	0.00
(6) $N_2O_5 + SO_2 \rightarrow SO_3 + N_2O_4$	−24	0.00
B. Organic Reactions Forming SO_3		
(7)  $\overset{O_3}{CH_2{-}CH_2} + SO_2 \rightarrow SO_3 + 2CH_2O$	−81	< 0.4–3.0
(8) $\cdot CH_2OO\cdot + SO_2 \rightarrow SO_3 + CH_2O$ $CH_2{=}O + O + SO_2 \rightarrow SO_3 + CH_2O$	~ −117 ~ −85	< 0.4–3.0
(9) $HO_2 + SO_2 \rightarrow HO + SO_3$ (a) $\rightarrow HO_2SO_2^\bullet$ (b)	−19 < −25	0.85 ?
(10) $CH_3O_2 + SO_2 \rightarrow CH_3O + SO_3$ (a) $\rightarrow CH_3O_2SO_2^\bullet$ (b)	−30 < −25	~ 0.16 ?
C. Reactions Forming $HOSO_2$ or $ROSO_2$ Radical		
(11) $HO + SO_2 \rightarrow HOSO_2^\bullet$	~ −82	~ 0.23–1.4
(12) $CH_3O + SO_2 \rightarrow CH_3OSO_2^\bullet$	~ −73	~ 0.48

TOTAL POTENTIAL RATE OF CONVERSION OF SO_2 TO SO_3 (OR SULFATES) IN MODERATE SMOG $\simeq$ 1.7 – 5.5% per hour

Table 6

Heterogeneous Reactions to Form Sulfate

A. Aqueous

(13) $SO_2 + H_2O(l) \rightleftharpoons H_2SO_3$

$H_2SO_3 \rightleftharpoons H^+ + HSO_3^-$

$HSO_3^- \rightleftharpoons H^+ + SO_3^=$

(13A) $2SO_3^= + O_2(aq) \rightarrow 2SO_4^=$

(13B) $SO_3^= + O_3(aq) \rightarrow SO_4^= + O_2$

B. Non-Aqueous

(14) $$\left.\begin{array}{l} SO_2\ (ads) \\ H_2O\ (ads) \\ O_2\ \ (ads) \end{array}\right\} + \text{Carbon(s)} \rightarrow H_2SO_4\ (ads)$$

that are sufficiently rapid to be of importance in the atmosphere, at least for polluted air with active photochemical processes. For comparison, estimates of the fractional conversion rate of SO_2 to $SO_4^{=}$ is given in the Table. These results are based on Calvert's computer simulations. These were based on an estimation of reactive intermediates after a 30-minute period of sunlight irradiation at zenith angle of 40°, with initial concentrations in ppm of NO_2 = 0.025, NO = 0.075, C_4H_8 = 0.10, CH_2O = 0.10, CH_3CHO = 0.06, CO = 10, CH_4 = 1.5, R.H. = 50% at 25°C, and SO_2 = 0.05-0.1.

The reactions (7) and (8) correspond to the interpretation of Cox and Penkett's (32) observations that SO_2 is oxidized at appreciation rates in the dark in ozone-olefin-air mixtures. The higher rate of 3% per hour was found for cis-2-pentene, while the lower rate of 0.4% $hr.^{-1}$ was found for propylene. Cox and Penkett suggested that either of two intermediates were involved in the SO_2 oxidation reaction. These are the ozonide reaction (7) or the zwitterion intermediates from the O_3- olefin reaction. The zwitterion has a diradical character and may be illustrated as reaction (8). Calvert's calculation of olefin-O_3 intermediates such as those in reactions (7) and (8) do not favor their importance as oxidizing agents. However, other radical species from the ozonide or zwitterion intermediates may be of interest, including those summarized by reactions (9 - 12). These classes of reactions may well account for SO_2 oxidation in the ozone-olefin mixtures.

Recently, the potential importance of radical addition reactions in the third class listed in Table 5 for SO_2 oxidation become more fully appreciated. Such reactions are exemplified in the series (9) to (12).

The rate of the HO_2 reaction has been made by Davis et al. (33). With such data, the fractional rate of SO_2 disappearance may reach ∿ 1% in a moderate photochemical smog. Assuming that the rate of the CH_3O_2-SO_2 reaction is the same as HO_2-SO_2 reaction, Calvert has estimated that the former will contribute a fractional oxidation rate of 0.2% hr^{-1} in moderate smog.

The OH radical-SO_2 reaction (11) appears to be of particular importance in the lower stratosphere where OH concentrations are estimated to be high (27,29). Calvert (21) has estimated the typical reaction rates for OH or CH_3 radical SO_2 reactions on the basis of analogies to reaction rates of CH_3, C_2H_5 and SO_2 reactions on the basis of analogies to reaction rates of CH_3, C_2H_5, and CFH_2CH_2. These rates are listed as 0.23% hr^{-1} and 0.5% hr^{-1} respectively at the lower range.

Measurements of the rate constant for the $OH + SO_2 + M \rightarrow HOSO_2 + M$ reaction are emerging from recent fundamental studies. Hamilton (34) has summarized the preliminary values of the rate constant for this reaction. At $\sim 300^{\circ}K$ the rate constant for this reaction ranges from Wayne's value of $\sim 7 \times 10^9$ M^{-1} for 1 atm Ar to (35) value of 1.1×10^8 M^{-1} sec^{-1} for 18 torr N_2 and 20 torr H_2O. Calvert (21) has used 1.1×10^9 M^{-1} sec^{-1} to estimate the upper limit of 1.4% hr^{-1} listed in Table 4.

This radical addition products, such as $HOSO_2$, should react rapidly with other species to generate sulfuric acid, peroxysulfuric acid, alkylsulfates and mixed intermediates such as $HOSO_2ONO_2$. Any of these ultimately should lead to sulfate in the presence of water.

Summing all of the known homogeneous reactions for SO_2 oxidation, it is possible to rationalize a theoretical rate of sulfate production in the range 1.7-5.5% hr^{-1} for moderate photochemical smog conditions. However, such rates are clearly highly dependent on the presence of unstable intermediates at relatively high concentrations. This is by no means a universal condition in non-urban air or in cities with minimal photochemical activity, as measured for example by ozone levels.

For conditions where photochemically induced homogeneous reactions cannot be important, the heterogeneous processes must be considered. The known reactions are listed in Table 6. These have been categorized as aqueous and non-aqueous reactions. The class of reactions that have been used most frequently to explain high SO_2 rates in the presence of liquid water containing aerosols in the system involving SO_2 absorption in water followed by oxidation by dissolved O_2 to form sulfate. Catalysis of the oxidation by heavy metal salts such as Mn++ ion can realize rates of oxidation in excess of 1% hr^{-1} in clean water solutions (e.g., Johnstone and Coughanowr (36), Matteson _et al_. (37). The absorption of SO_2 can be promoted by the buffering effect of simultaneous absorption of ammonia. Scott and Hobbs (38) have shown that the aqueous SO_2 oxidation process can be enhanced significantly by ammonium ion. Indeed the estimates and experiments of Miller and dePena (39) and Corn and Cheng (40) suggest that rates of SO_2 oxidation can be achieved in fog approaching 10% hr^{-1}.

It is well known that ozone is quite soluble in water. Therefore, one expects that ozone absorption with SO_2 would contribute to significant oxidation of SO_2. Experiments of Penkett (41) have shown that oxidation of SO_2 in air at 7 ppb absorbed in water droplets with ozone, present in surrounding air at 5 pphm, can be as large as 13% hr^{-1}. Thus, foggy or cloudy air mixed with photochemical smog, such as sometimes observed along the Pacific Coast, could well be an important medium for $SO_4^=$ formation. Furthermore, such an aqueous mechanism could be significant at middle altitudes over continents even at background ozone levels.

The reported rates of SO_2 oxidation in clean water droplets must be considered maximum. It is questionable whether they ever can be achieved in the atmosphere since such aqueous reactions have been shown to be suppressed significantly by organic contaminants. The work of Fuller and Christ (43) and later of Schroeter (44) has indicated the aqueous absorption of SO_2 and its subsequent oxidation is reduced as much as an order of magnitude by dissolved organic acids or alcohols. This type of material is known to be present in the atmospheric aerosol sampled at the ground, so one can expect that the aqueous oxidation will probably be most efficient in relatively clean conditions of clouds well away from the earth's surface.

The heterogeneous mechanisms of SO_2 oxidation in the absence of liquid water are poorly understood. However, the recent work of Novakov et al.(42) has shown that $SO_4^=$ can be produced rapidly on the surface of carbon particles suspended in water vapor and air. These workers have observed that significant amounts of $SO_4^=$ can be found on carbon particles generated by combustion of hydrocarbons in ppm level SO_2 enriched air.

It is difficult to assess the significance of carbon or organic particles for the SO_2 oxidation in the free atmosphere. There is little doubt that absorption of SO_2 on carbon particles freshly generated by combustion can provide a surface catalyzed oxidation medium. Indeed experiments such as those of Yamamoto et al. (45) have shown that SO_2 oxidation can be as high as 30% hr^{-1} on activated charcoal particles 5 mm in diameter. Their work also indicates that this rate is strongly reduced by sulfuric acid collection in the mocropores of the charcoal. The work of Yamamoto et al. further emphasizes that such a heterogeneous oxidation mechanism depends on a variety of factors, ranging from grain size of the carbon, temperature, concentration of SO_2, H_2O vapor, and oxygen, as well as the micropore structure of the particle surface. It would seem that oily, gummy, wet particles collected from the atmosphere would be poorly suited for non-aqueous reactions to form sulfate since their micropore structure would be minimal. Yet such a mechanism cannot be ruled out from consideration at this time.

Nitrate Forming Reactions

Like the production of sulfates, nitrates in atmospheric aerosols can be formed by a wide variety of homogeneous reactions as well as heterogeneous reactions. The pathways of nitrate generation are less well understood than sulfate, but it is likely that they are interrelated at least in some circumstances.

Since both nitrous acid and nitric acid are much more volatile than sulfuric acid, it does not appear possible that particulate nitrogen oxide species will exist in the atmosphere in pure form as acids. Thus the production of nitrate must involve formation of a condensable species such as NH_4NO_3 in the gas phase, or the absorption of a nitrogen oxide constituent for particles followed by stabilization through chemical reaction. Such heterogeneous processes, of course, can take place in an aqueous or non-aqueous medium.

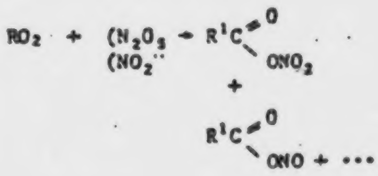
The precursors for particulate nitrate formation are summarized in Table 7. These are classified in terms of (a) important nitrogen oxides, (b) volatile acids HONO, and $HONO_2$, and (c) gaseous nitrates.

Because nitric oxide is relatively insoluble and nonreactive with water, the important nitrate forming atmospheric oxides of nitrogen are believed to be NO_2, NO_3, and N_2O_5. These species are formed mainly in the atmosphere by the well known "smog" reactions (16 - 20) and are not emitted primarily from material or anthropogenic sources.

With the nitrogen oxides coexisting with water vapor and sulfuric acid, the volatile nitrous and nitric acids can be formed via the reactions (21 - 24). The mixed intermediates involving sulfuric

Table 7

Reactions Potentially Involved in Nitrate Formation

Species	Rate Constants ($ppm^{-1}min^{-1}$)*
A. Nitrogen Oxides	
(15) $O_3 + NO \rightarrow NO_2 + O_2$	21.8
(16) $O + M + NO \rightarrow NO_2 + M$	
(17) $RO_2 + NO \rightarrow NO_2 + R^1CH$	
(18) $O_3 + NO_2 \rightarrow NO_3 + O_2$	
(19) $NO_3 + NO_2 \rightleftharpoons N_2O_5$	
B. Volatile Acids	
(20) $N_2O_5 + H_2O \rightarrow 2\ HONO_2$	2×10^{-5}
(21) $HO + NO_2 + M \rightarrow HONO_2 + M$	10^{-5} (M = 1 atm N_2)
(22) $NO + NO_2 + H_2O \rightarrow 2\ HONO$	
(23) $HOSO_2O + NO \rightarrow HOSO_2\ ONO$ $+ H_2O \rightarrow H_2SO_4 + HONO$	
(24) $HOSO_2O + NO_2 \rightarrow HOSO_2\ ONO_2$ $+ H_2O \rightarrow H_2SO_4 + HONO_2$	
C. Gaseous Nitrate	
(25) $NH_3 + HONO_2 \rightarrow NH_4NO_3$	~ 10^{-6}
(26)  $RO_2 + \left(\begin{array}{l}N_2O_5\\NO_2^{\cdot\cdot}\end{array}\right. \rightarrow R^1C\begin{array}{l}{}^{\nearrow O}\\{}_{\searrow ONO_2}\end{array} + R^1C\begin{array}{l}{}^{\nearrow O}\\{}_{\searrow ONO}\end{array} + \cdots$	10

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*Typical for smog reactant concentrations.

acid are of interest as they link the NO_x and SO_x chemistry. Once the volatile acids are formed, they may react with ammonia in the gas phase to form, for example, NH_4NO_3 (reaction 25). The nitrogen oxides also react with radicals such as RO to form organic nitrates and nitrites including peroxy acetylnitrate (PAN). Reaction (26) has been hypothesized by Calvert (21) on the basis of analogy to the NH_3-HCl reaction. For concentrations of NH_3 and $HONO_2$ at ∿ 1 pphm, Calvert's (21) work suggests that the ammonia reaction may represent a significant removal path of $HONO_2$ to form aerosols.

It is possible that condensable organic nitrates are formed via reaction (26) in the gas phase. Certainly the observation of such materials from smog chamber experiments (O'Brien et al. (46)) would provide some evidence for such cases. However, it is known that volatile organic nitrates such as PAN readily hydrolyze in an aqueous medium to form nitrite ion (Reaction 31). Thus the presence of such compounds resulting from gas phase reactions could lead to particulate nitrate after stabilization with ammonium ion or another cation.

Of the gas phase reactions involved to form nitric acid vapor, (20) and (21) are believed to be most important. Using currently accepted rate constraints for these reactions, Calvert has estimated that

$$R_{20} \approx 0.5\text{-}2 \times 10^{-5} \text{ ppm min}^{-1}$$

$$R_{21} \approx 2\text{-}6 \times 10^{-5} \text{ ppm min}^{-1}$$

in moderate photochemical smog. Thus, it would appear that reaction (21) is of principal importance for $HONO_2$ formation in smog. The rate of conversion of NO_2 to $HONO_2$ by this reaction should be in the range of 2-8% hr^{-1} for the conditions used in the calculations in Table 5 (21). With absorption in wet aerosols and neutralization with ammonium ion, this is not unreasonable for the upper limit of estimated nitrate formation rate in Los Angeles smog in the morning "peak" condition. Once the nitrogen oxides are present or the acids begin to form, the interaction of these species with moist aerosols can take place. Some potentially important reactions are given in Table 8. Here the complexities of the aqueous reactions of NO_x become apparent. All of the nitrogen oxides contained in the atmosphere will react with liquid water to form traces of nitrate and nitrite. These reactions are generally reversible, however, so that the anions must be stabilized by a base such as NH_4^+. In the presence of dissolved oxygen or ozone, nitrite ion can be oxidized to nitrate in analogy to the aqueous sulfate formation reactions.

None of the nitrate reactions has been studied with atmospheric application in mind. However, there is a variety of information in the chemical literature dealing with NO_x absorption in water. There is ample evidence, for example, from studies reported by Nash (47) and Borok (48) that NO_2 at trace levels in air is readily absorbed in aqueous solutions. The efficiency of absorption varies widely, however, depending on the acid-base content of the solution.

If significant quantities of concentrated sulfuric acid are formed in atmospheric aerosols, nitrate formation via absorption of NO_2 to form nitrosylsulfuric acid, $HNOSO_4$, may be of interest.

The rate of absorption of NO_2 in sulfuric acid is fast, but the efficiency appears to be relatively low, according to Baranov _et al_. (49). Again it appears that ammonia absorption or another base has to be involved to drive the equilibria to nitrate production. Thus, in all of these aqueous reactions, nitrate formation may be limited by the concentration of ammonia rather than by any of the nitrogen oxide species.

Organic Particle Formation

Of the three major contributors to secondary aerosol production, the least is known about mechanisms for the organics. These processes have not been identified with any certainty yet. It is

Table 8

Aqueous Reactions of Nitrogen Oxides

(27) $N_2O_5 + H_2O(\ell) \rightarrow 2H^+ + NO_3^-$

(28) $NO + NO_2 + H_2O(\ell) \rightarrow H^+ + NO_2^-$

(29) $2NO_2 + H_2O(\ell) \rightleftharpoons H^+ + NO_3^- + HONO$

$HONO + OH^- \rightarrow H_2O + NO_2^-$

(29a) $2NO_2^- + O_2\ (aq) \rightarrow 2\ NO_3^-$

(29b) $NO_2^- + O_3\ (aq) \rightarrow NO_3^- + O_2$

(30) $2NO_2 + H_2SO_4 \rightleftharpoons HNOSO_4 + HNO_3$

$HNOSO_4 + H_2O(\ell) \rightleftharpoons HNO_2 + H_2SO_4$

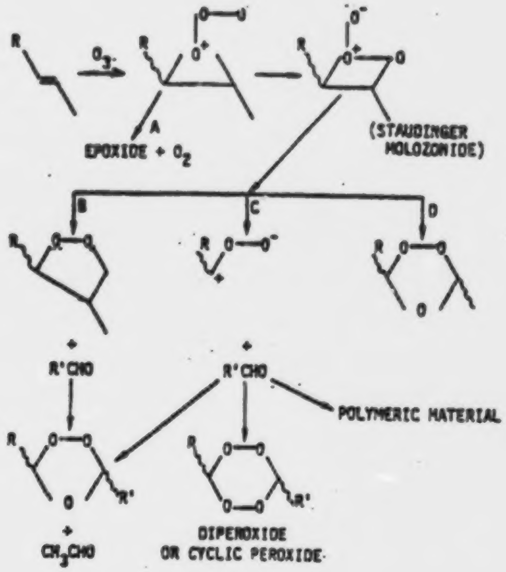
$3HNO_2 \rightleftharpoons HNO_3 + 2NO + H_2O$

(31) $RONO_2 + H_2O(\ell) \rightarrow H^+ + NO_2^- + R'OH$

possible that organic materials can be polymerized in sulfuric acid solutions, for example. However, it is known that such reactions generally take place in very strong acid above 90% concentration. At equilibrium with water vapor in the lower atmosphere, H_2SO_4 should not exceed 40% concentration in water. Another possible class of important organic aerosol reaction involves the attack of ozone on olefins.

The ozone-olefin reaction mechanism remains a subject of controversy. One approach that can serve to illustrate the broad features of the reaction as related to aerosol formation is Story's model as shown below (see next page). The ozone adds to the olefinic band forming zwitterion, which can result in an epoxide or a molozonide. These species can follow one of three added paths to generate condensable peroxides or polymeric material. Addition of water in the system can provide added paths for decomposition of the peroxides to form acids or other oxygenated species including alcohols and aldehydes. All of these materials have been identified in atmospheric aerosols.

The intermediates identified by Cox and Penkett (32) appear in the early stages of the ozone-olefin reaction and offer a potential link between the sulfate chemistry and the organic aerosol chemistry.



The recent experiments of Burton et al. (50) have shown that the ozone- (terminal) olefin mechanism for aerosol production is initia-ly first order in ozone and olefin. The constant relating the rate of maxx concentration change increases with carbon number of the olefin. The significance of this effect is illustrated in the data shown in Fig. 9. Here the experimental variation in generation of condensable material from the reaction between ozone and several terminal olefins is shown for an ozone concentration of 12 ppm. Significant production of aerosol is observed over a reaction time of 54 seconds mainly for the larger molecular weight species.

The empirical rates of production of aerosol from dry air ozone-olefin mixtures are shown in Table 9. Extrapolation of these data to olefins at the ppb level and ozone of 10 pphm suggests a production rate of tenth's of $\mu g/m^3$-hr. of organic material, which is an order of magnitude lower than projected from atmospheric observations in Los Angeles. Thus, either the estimate of total precursor concentration is too low, or the ozone-olefin mechanism cannot explain the atmospheric processes. It is also interesting that the experiments of Burton et al. (50) have demonstrated that aerosol formation in such mixtures using 10 ppm O_3 and 10 ppm hexene in dry air is heavily influenced by the addition of water vapor. Furthermore, traces of butyraldehyde strongly inhibit the formation of aerosols in this system.

This work suggests that the ozone-olefin reactions or oxygen atomolefin reactions may be important. These classes of reactions involving high molecular weight olefins are known to produce polymerized oxygenated species that will condense out at ppb vapor concentrations. For carbon number greater than six, yields of polymerized material should exceed several percent of the vapor concentration. Such reactions are likely to be promoted on particle surfaces when the surface of large particles could act as a preconcentrator for the olefin or air intermediate species.

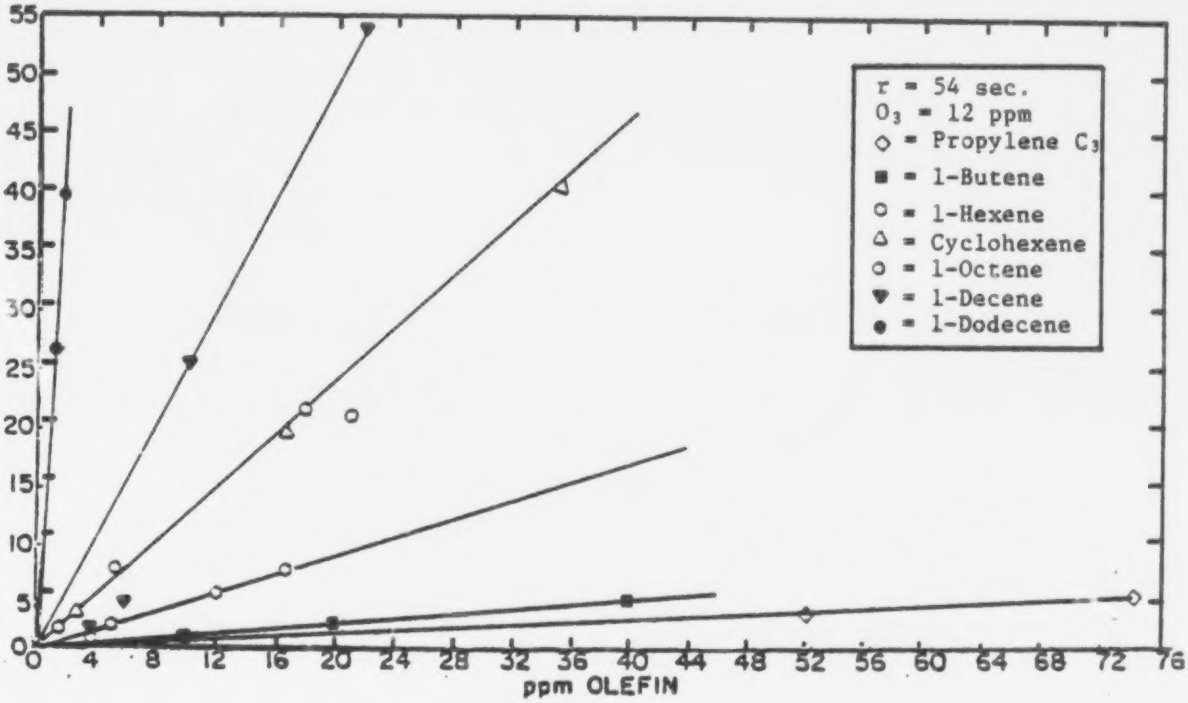


Figure 9. Mass Concentration of Aerosol Formation for Olefin-Ozone Reaction as a Function Olefin Concentration.

Table 9

Empirical Rate Relationships for Ozone-Olefin Reactions

Olefin	Rate ($\mu g/m^3$-sec-ppm^2)
Propylene	1.0×10^{-2} ($\pm 0.3 \times 10^{-2}$)
1 - butene	1.7×10^{-2} ($\pm 0.5 \times 10^{-2}$)
1 - hexene	6.0×10^{-2} ($\pm 2.0 \times 10^{-2}$)
1 - octene	18.0×10^{-2} ($\pm 6.0 \times 10^{-2}$)
1 - decene	37×10^{-2} ($\pm 18 \times 10^{-2}$)
1 - dodecene	4.0 ($\pm$ 1.0)
cyclohexene	18.0×10^{-2} ($\pm 6.0 \times 10^{-2}$)

C. Application of Laboratory Simulation.

The review of potentially significant reaction mechanisms to form atmospheric aerosols could be an endless challenge for the chemist. Basic laboratory experiments to determine rate constants and important reaction steps play a key role in eliminating many candidates. However, the complexities of the chemical interactions in atmospheric processes cannot be elucidated by fundamental experiments alone. The predictions of behavior of reactive mixtures should be consistent with atmospheric processes or with atmospheric simulation experiments. Simulation of atmospheric phenomena using the study of controlled laboratory prototypes is a well known technique, particularly as applied to fluid dynamic processes. However, the simulation of atmospheric chemical phenomena is less well established. With the possible exception of the work of Friend et al.(3), only simulations of the lower atmosphere, more specifically urban air, have been attempted. The principal method that has been used by many investigators is the static reactor or smog chamber approach, where air mixtures containing reactive contaminants are studied over a several hour period. Such studies are known to duplicate qualitatively, at least, many of the features of urban photochemistry to form ozone and other smog products. The principal deficiencies as simulators include the low volume to surface ratio compared with the atmosphere, and the uncertainty in the roll of wall reactions.

A limited number of smog chamber experiments have been undertaken to investigate aerosol formation in smog. Aside from the early studies reviewed by Leighton (1), these include those of Groblicki and Nebel (51), Wilson and colleagues (52, 53, and 54), O'Brien et al.(46), and the CALSPAN group (53). The results of these studies generally confirm that significant aerosol formation in simulated smog requires an induction time until ozone begins to build up, reflecting the time required for build up of reactive intermediates such as HO, HO_2, RO_2, $HONO_2$, etc. from chain reactions involving olefinic hydrocarbons. Aerosols found in chamber experiments are composed of oxygenated organic material including carboxylic acids and organo-nitrates. If SO_2 is present, sulfate also is found. Much of the nitrate generated appears to be accumulated on the walls of the chambers.

The presence of SO_2 in irradiated NO_x-hydrocarbon-air mixtures enhances aerosol formation, but does not significantly influence the ultimate ozone level realized in the chamber. With a suitable choice of rate constants for reactions of HO and SO_2, and HSO_3 to form $SO_4^=$, Calvert (21) has indicated that computer modeling can duplicate many features of the Battelle chamber experiments (e.g., Wilson and Levy (52)).

The smog chamber studies have been useful in classifying the reactivity of hydrocarbons for photochemical aerosol production. With SO_2, the experiments generally indicate that the terpeniod compounds such as α-pinene are highly prolific aerosol formers followed in rough order by di-olefins, cyclic olefins, high molecular weight terminal olefins and aromatics. Without SO_2, the work of O'Brien et al.(46) suggests that only diolefins and cyclic olefins of carbon number six or greater will generate significant quantities of aerosol at atmospheric pollutant concentrations for NO_x. Unfortunately such compounds have not been identified in air or in sources like motor vehicle exhaust. Their work also suggested that NO_2 tended to suppress aerosol formation. In another study using a smog chamber, Ripperton et al. (56) has given evidence for the importance of ozone attack on an olefinic bond in aerosol formation, particularly in "natural" production from terpenoid compounds.

To minimize the interactions between gases and the containing walls, another approach to simulation of aerosol forming reactions has been attempted recently. Lipeles et al.(57) have reported a steady flow reactor technique in which the initial reactions of aerosol formation in irradiated gas mixtures are studied at reactant concentrations approaching those in the atmosphere. The initial experiments employing the flow method have demonstrated the nuclei can be generated in irradiated gas mixtures containing traces of NO_2 and olefins ($<C_6$) over 10 second residence times. Their studies also have indicated a somewhat different reactivity scale than the smog chamber work. Although α-pinene was the most prolific particulate generator, high molecular weight terminal olefins and the conjugated hexadiene were superior to cyclohexene in aerosol production. The experiments of Lipeles _et al_.(58) further show that independent addition of SO_2 at ppb concentrations and NH at ppm concentrations to the reaction mixtures enhance aerosol production. Their work showed no consistent relation with NO_x concentrations; however, water vapor clearly suppressed aerosol formation in the flow reactor system. This observation is consistent with the smog chamber studies of Groblicki and Nebel (51), but raises questions about Wilson's conclusions (60) about the importance of stirring as the inhibiting influence of humidity.

To our knowledge, only one of the simulation studies so far has attempted to duplicate the effect of existing particles in the reacting gas mixtures. Only by the addition of particles under controlled conditions can the relative significance of heterogeneous reactions and homogeneous reactions be deduced. In the preliminary work of Heisler and colleagues (59) at Cal Tech, a study has been made of the nucleation and growth of aerosols in irradiated air mixtures doped with cyclohexene. These experiments have revealed that both nucleation and growth can take place in a medium containing $\sim 10^4$ particles per cm^3. In this case, the growth of particles appears to be consistent with a vapor diffusion controlled process influenced by the radius of curvature effect on vapor pressure.

4. INTERPRETATION OF PRESENT KNOWLEDGE

The results of a large number of laboratory experiments and their interpretation provide strong evidence for the potential importance of several mechanisms to produce atmospheric aerosols. The processes are clearly complicated with many possible interacting avenues for formation of sulfate, nitrate, and organic material. However, the results of smog chamber simulations leave little doubt that photochemistry must play a role in aerosol evolution. At the same time, heterogeneous processes involving liquid water droplets or moist aerosols certainly are key factors, at least in the troposphere. The evidence for non-aqueous heterogeneous reactions is less compelling at this time, but they cannot be ruled out as factors in the particle-gas interactions expected to take place in the atmosphere.

Until recently, the details of the changes in atmospheric aerosols over short time periods were unknown so that meaningful intercomparisons between the atmospheric prototype and our mechanistic models could not be undertaken. With the results of new field experiments such as the ACHEX in hand, the significance of different mechanisms can now be tested, at least for urban air.

A. Sulfate Formation.

In the case of photochemical smog in Los Angeles, comparison of the observations with expectations of chemistry suggest qualitatively that several mechanisms probably play a role in sulfate and nitrate formation. The evidence is strong that submicron sulfate particles are produced photochemically as a part of the smog mechanism. Such formation is coupled closely with the changes in organic aerosol during the day and is well correlated with the delay required to produce the high levels of oxidant.

The reactions that appear to be most significant for submicron sulfate are homogeneous in nature, either involving a dark reaction of ozone and olefins, or the groups of free radical reactions such as OH attack on SO_2. The accumulation of sulfate on the submicron particle fraction during the day is consistent with a vapor diffusion limited process with a condensable or reactive precursor such as H_2SO_4 or HSO_3 radical. An alternate mechanism of catalytic SO_2 oxidation on carbon particles may be significant, but in our opinion it is a less likely mechanism than the photochemically related processes, or reactions involving an aqueous medium.

The behavior of sulfate in the larger particles shows a poorer correlation with ozone and carbon in Los Angeles air, but the correlation with relative humidity change is also weak. It is likely that aqueous sulfate formation mechanisms play some role in total sulfate behavior in Los Angeles, particularly at night or in conditions of fog or haze with high liquid water content. Incidentally, the liquid water content of the Los Angeles aerosol varies with total mass concentration more strongly than relative humidity (61). The inhibiting influence of organics in aqueous urban aerosols is uncertain, but may be a factor in the apparent variability of sulfate generation from day to day in Los Angeles.

Extrapolation of the experience in Los Angeles to other situations in the troposphere is difficult because a lack of suitable observational data. However, it is likely that the photochemical formation of sulfate will begin to be important whenever ozone exceeds 0.1-0.2 ppm in air and reactive hydrocarbons are present. At the ground, the reactions in aqueous media are likely to be important in both urban and non-urban air if photochemically induced processes are absent. Away from the ground in the middle and upper troposphere, reactive hydrocarbon and free radical concentrations should be rather low under most circumstances. The presence of organics in aerosols at cloud level and above should be minimal so that the aqueous oxidation processes globally should play a dominant role between 2 km and 10 km altitude.

In the lower stratosphere, the reactions of principal interest for sulfate formation appear to be photochemically induced. In particular, the homogeneous reaction of OH and SO_2 seems to be the leading candidate for $SO_4^{=}$ formation at this time.

B. Nitrate Formation.

The knowledge of nitrate forming processes applicable to the atmosphere provide a less convincing basis for explaining the behavior of this ion than that of sulfate. The key difference in mechanisms evidently is centered around the volatility of nitrous and nitric acid and their equilibria in aqueous solution. The Los Angeles experience emphasizes the distinct difference in nitrate evolution as compared with sulfate. There appear to be two extremes of behavior, first a short term transient production accompanying the NO_x peak in the morning and second a much slower, but systematic production such that high concentrations of NO_3^- appear after two to three hours of air mass transport across the Los Angeles Basin. The overall NO_3^- production correlates poorly with ozone, NO_x, and NO_2, but the transient peak in the morning takes place at high relativel humidity.

The evidence suggests that nitrate could be generated via homogeneous gas phase reactions or by hetrogeneous, aqueous processes. It seems that intermediate species other than NO_2 are involved at least during the morning transient period. The independence of the nitrate conversion ratio on NO_2 or NO_x may suggest a droplet rate controlled NO_3^- formation after absorption. The complicated equilibria involved in nitrogen oxide ion solutions underscores the potential importance of basic substances such as NH_4^+ necessary to neutralize acidic particles. It is likely that NH_3 plays a critical role in stabilizing nitrate in aerosol particles. This conclusion can be drawn from the Los Angeles experience since there are relatively high ammonia concentrations in air over the eastern parts of the Basin where the highest nitrate levels are observed.

Interpretation of nitrate formation in the troposphere is difficult at present because of the paucity of atmospheric aerosol data. However, it is likely that photochemical processes are important since the highest nitrates are generally observed in cities with high oxidant levels, particularly in Los Angeles. Again it would seem that NH_3 plays a crucial role in nitrate generation if acids are involved. Thus one would expect that less nitrate would be present at higher altitude away from the principal sources of NH_3.

The absence of NO_3^- in stratospheric aerosols appears to be related to the high volatility of HNO since this species has been observed as a gas at altitudes above 15 km.

C. Organic Carbon.

Organic material is almost universally present in tropospheric aerosol samples but is probably absent from stratospheric material. The presence of organics in aerosols can be attributed to primary natural and anthropogenic sources, as well as to secondary processes in the atmosphere. The details of the secondary reactions are essentially unknown, but an important candidate based on laboratory studies is the ozone reaction with cyclic or linear olefins of carbon number larger than approximately six. The principal limitation in producing organic aerosols in the atmosphere appears to be the vapor pressure of condensable species.

The data taken in Los Angeles indicate that most of the non-carbonate carbon found in smog aerosol is secondary in nature. It is made up of a substantial amount of oxygenated material with some organic nitrate present. The organic reactions yield mainly sub-micron particles; production seems to correlate well with changes in ozone as well as with sulfate. In Los Angeles the organic fraction is normally the largest contributor by mass to filter collected aerosol samples.

The concentration of organics in the submicron particle fraction provides circumstantial evidence for a gas phase formation reaction followed by vapor diffusion controlled growth on existing particles. The presence of significant quantities of oxygenated material and the correlation with ozone buildup are consistent with the expectation that ozone-olefin reaction is important.

At this time, there is virtually no information on the composition of olefins greater than C_6 in the ambient atmosphere so that the organic aerosol precursors cannot be considered as known in urban air. However, taking a difference between the non-methane hydrocarbon vapor concentration and the $<C_6$ hydrocarbon fraction identified by chromatography suggests that the $<C_6$ fraction may be about half of the NMHC concentration. Thus it is reasonable to expect that several high molecular weight olefins are present at ppb levels in urban air.

Near the ground, vegetation emanates significant quantities of hydrocarbon vapors. Thus organic aerosols can readily be formed in non-urban air from reactions between "background" ozone and such compounds as the terpenes from evergreens.

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PARTICULATE MATTER IN THE ATMOSPHERE

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PARTICULATE MATTER IN THE ATMOSPHERE

Irrespective of the very real hazards posed by gaseous pollutants, it is clear that, from the public viewpoint, the most evident air pollutant is suspended particulate matter. Airborne particles obscure visibility and change the color of the sky. The unaided sense of sight thus documents the presence of particulate pollutants wherever they occur. It is probably that only malodors among the other pollutant species are as clearly detectable or as likely to produce public outcry.

For example, it is probably safe to assert that the entire present pressure to remove sulfur dioxide from power plant stack gases, almost irrespective of emitted concentrations, was triggered by the highly visible particulate plume from the Four Corners power plant. The truth of this statement is difficult to document precisely, but a general reading of the popular news media strongly suggests its truth. Had the Four Corners plant been originally constructed with adequate air cleaning equipment so that visible emissions were minimized, it is highly unlikely that the entire present pressure to remove sulfur dioxide as well could ever have been mounted. In fact, the public is eager to confuse pollution with sensory impressions. Local newspapers have received quantities of letters protesting "the unbearable order of carbon monoxide in the streets," and "the poisonous air in the _____tunnel; you could hardly see for 200 feet.

In addition to adverse public reactions, effects of suspended particulate matter fall into the following categories.

(1). So called "nuisance dust." Generally speaking, this is used to refer to the actual soiling of surfaces, primarily by settlable dust. These are very large particles with significant falling velocities in still air. The name is to some extent a misnomer, since settled dust imposes a specific economic impact by increasing the necessary frequency of cleaning whatever surface it lands on.

(2). Decreased Visibility. Two cases must be distinguished. The acute visibility decrease characteristic of duststorms and extremely high pollutant levels can have an immediate impact through increased accident rates and airport closings. At far smaller particulate concentrations, the inability to see distant objects and the sky discoloration has an esthetic impact that may well translate into economics. That is to say, there are indirect impacts including psychological depresssion that may decrease individual productivity, depreciation of real estate values, or, in the case of tourist areas, a major disruption of tourism because of the impairment of particular scenic vistas. Values of this sort can well change with time; what is today a tolerable degree of visibility of impairment may become intolerable when highlighted by the erection of a highly visible landmark building, an elevated roadway that allows longer views than are possible in street canyons, or even the establishment of the new park that affords previously unavailable view over the city.

(3). Pneumoconioses. Certain specific particulate species cause specific health effects that are adequately documented as to etiology. Obvious examples are silica, asbestos and beryllium. There are certainly other specific physiological responses that will also be documented in the near future.

(4). Epidemiological Effects. There is a sizable body of information showing a coincidence between high particulate concentrations and morbidity. There is at the moment no etiological connection between the two. Taking the data at face value, it is possible to hypothesize (a) that high particulate concentrations cause illness; (b) that some fairly ubiquitous component in the particulate matter causes illness; (c) that some non-particulate species that tends to vary in the same sense as particulate matter causes illness; or (d) that sick people emit particulate matter. While external physical considerations made (d) above unlikely, there is insufficient basis for choosing among the other three alternatives.

Despite the uncertainties involved, the National Air Quality Standards for particulate matter were based on the epidemiological relationships cited above, and the secondary standards primarily on the esthetic effects; a partial concentration of 60 micrograms per cubic meter corresponds, on an average, to a visibility of approximately 20 kilometers.

It should be noted that the different effects generally derive from different portions of the size spectrum of particles. Particles larger than a few microns are inhaled to a negligible extent, and are hence of minor concern as lung irritants. On the other hand, very large particles can settle on vegetation and cause toxic effects by subsequent ingestion. The most efficient sizes for obscuration of visibility are in the range between 0.1 and 1 micrometer, but very large particles, if present in sufficient concentrations, can obscure visibility very effectively. Particle size range during duststorms is very large indeed. Particles below 0.1 micrometer are least effective in decreasing visibility. Nuisance dust, as noted previously, is nearly all larger than about 5 micrometers.

Generally speaking, particles larger than one micrometer are produced by mechanical processes, while particles smaller than that limit are produced by condensation from the gas phase. This means, among other things, that there are significant differences in particle composition, with the break point for most of these occurring somewhere near one micrometer. Since a number of the effects also differ for particles above and below that limit, there has been pressure to create different and separate standards for particles above and below that limit.

Still more recently, with the availability of increasing complete analyses of atmospheric particulate matter, it has become clear that, in some cases, a significant portion of the total particulate loading of the atmosphere is caused by conversion of gaseous pollutants to particles. Species that enter the atmosphere in the particulate state are generally referred to as primary particulate pollutants; those resulting from gas to particle conversion subsequent to emission are called secondary. The rather high fraction of secondary pollutants found in some atmospheres has raised the question as to whether greater gains may be made in reducing ambient particulate concentrations by controlling the primary emissions, or by controlling those gases that create the secondary pollutants.

In this report, primary emphasis will be given to two questions: (1) the relative effectiveness, on a national basis, of controlling primary particulate emissions as against controlling those gases that produce secondary particulate matter; and (2) the possible restructuring of the National Air Quality Standards on the basis of particle size or of other considerations.

SOURCES OF ATMOSPHERIC PARTICLES

Before proceeding to answer these questions, it is necessary to understand the source of the particulate matter found in cities, and for that matter, in remote locations. This has been nicely schematized by Friedlander (1973). By a series of regression formulas, Friedlander was able to account for a very large fraction of the particulate matter collected at a site in Pasadena, California, by considering only 12 sources, although not all of these could be completely resolved. Harrison, et al. (manuscript, source unknown) apparently accounted for a very large fraction of suspended particles in Chicago and an even smaller number of categories. Unfortunately, similar regressions or other exhaustive treatments have not been undertaken for other cities.

Sources of Particles Larger Than One Micrometer. As noted previously, the bulk of the larger particles are produced mechanically. In most areas, the major single source of such particles is the soil, with the mineral industries and other grinding processes generally supplying most of the balance. Depending on location, there may also be a significant component of marine aerosol in this size range. However, numerous studies have shown that the surface concentration of marine aerosol decreases rapidly with distance inland, and this should be an important component only in coastal cities. In general, the industrial component of this size fraction contains few surprises. Whenever material is pulverized, some fraction of it generally escapes to the atmosphere and will be found in samples taken at a suitable location. A flour mill will produce starch particles, a cement plant will produce particles of cement, an iron foundry bits of rust, and so on through the list. In addition, the movement of traffic will provide particles of both the road surface and of rubber tires.

One of the most generally underrated components of this largest size fraction is soil and associated materials, including bits of pulverized vegetation in the appropriate seasons. Under many circumstances, this can make up more than half of the total mass of particulate matter. Lodge, et al. (196) showed that roughly one-fifth of the carbon in a series of large samples from St. Louis, and nearly twice that amount in a single Los Angeles sample were contemporaneous carbon, based on carbon 14 content. The bulk of this was in the portion of the particulate matter that was insoluble in ether. Unfortunately, there was no separation by size in the samples, but the most likely interpretation would be that an important portion of the organic matter consisted of spores, micro-organisms, pollens, and comminuted plant material. Unfortunately, this work seems not to come to the notice of those presently attempting to make elementary balances on more recently collected samples.

There is a strong temptation to regard soil particles as "natural" pollutants. In fact, this is rather infrequently the case. There are very few situations in which quantities of dust become airborne from soil that is in the totally undisturbed natural state. However, in many situations, the natural vegetation cover is extremely fragile, and the passage of only a few people or vehicles is enough to destroy it. At this point, then the soil becomes very susceptible to wind erosion. There is good evidence that even as vast an area of denuded soil at the Sahara Desert is probably originally anthropogenic. Unfortunately, the recovery rate of such soil, once disturbed (in this case by over-grazing) is on the time scale of millenia.

Hagen and Woodruff (1973), among others, have shown that wind entrainment of soil has a rather abrupt onset at approximately 7 meters per second wind speed. This offers the possibility of differentiating aeolian dust from other components by segregating measurements made at higher wind speeds. That even this strategy is not completely successful will be shown later. In addition, of course there is undoubtedly a significant portion of dust stirred up by vehicle motion on unpaved roads and streets, in unpaved parking lots, and by other related mobile activities.

Particles Smaller Than One Micrometer. Whitby and his group (see, for example, Willeke, et al. (1974) have shown that the submicron aerosol is generally bimodal in size distrubiton. One mode, usually in the vicinity of 0.02 micrometers, represents the initial size distribution of particles formed by rapid condensation from the vapor state in thermal processes. For example, the bulk of the lead compounds from leaded gasoline combustion enter the exhaust system in the vapor state and condense during the transit through the exhaust system, or within a very short distance of the end of the auto tailpipe. Metallurgical fumes and soot from incomplete combustion probably also begin in this size range. However, at this very small size, the amplitude of brownian motion is large and the concentrations at the source are rather high. As a result, rapid coagulation is apt to occur, giving rise to the second mode at about the point at which brownian motion becomes unimportant--at ordinary atmospheric pressures, somewhere in the decade of size immediately below one micrometer. Whitby's group refers to this second mode as the "accumulation size range," for fairly obvious reasons, and considers its predominance to indicate an aged aerosol mass. While interactions between this size range and the large particles unquestionably occur, their rates of diffusion are sufficiently small that it an infrequent affair, and does not constitute, on the time scale of air travel over a moderate sized city, any significant cause for depletion of the accumulation mode, nor for particle growth in the large size range. One exception is the case in which the fume material is temporarily deposited on the surface and then later reentrained. For example, an automobile that has been operated for a protracted period at low speed accumulates a certain amount of lead in its exhaust system. If it is then taken up to highway speed, this deposited lead is mechanically discharged in large particles. Similarly, soot deposited in chimneys can be blown loose in flocs that are large enough to be visible by the naked eye.

This size range will also include organic materials such as lubricating oils that are vaporized at high temperature and condense on subsequent cooling, precisely analogously to the inorganic species as described above. Such materials are generally high in carbon and low in hydrogen and, at least when fairly recently emitted, contain negligible amounts of oxygen.

Secondary Aerosols. The work of Goetz and Pueschel (1965) suggests that the formation of secondary materials by the photochemical reaction of organics and nitrogen oxides ("The Los Angeles Smog" reaction) occurs preferentially on surfaces of pre-existing particles. It further suggests that the extent of reaction is rather proportional to the available surface. Whitby, et al. (1975) have shown that nearly all of the surface in a typical Los Angeles air sample is in the submicrometer size range. Growth on the very smallest particles may be somewhat inhibited by Kelvin effect, but it is still to be expected that most of the growth of organic secondary aerosols will occur on the submicron particles.

Inorganic secondary aerosols are predominately sulfates and nitrates; they also seem to occur predominately in the submicrometer size range. Less is known concerning their precise distribution, particularly in the very smallest sizes. However, it should be noted that the converse statement cannot be made--that all sulfates and nitrates are secondary. In the first place, some sulfate and nitrate are probably formed by interaction of the corresponding gases with existing particles to displace such appropriate anions as halide. Since there is very little change in particle mass or other characteristics, it is probably not completely proper to refer to such metamorphosed particles as secondary. In the second place, soils in many parts of the country contain gypsum and other sulfate minerals, as do a number of commercial fertilizers and other industrial materials. Thus some fraction of many sulfate samples may be primary. The matter will be further discussed below.

RELATIVE CONTRIBUTION OF PRIMARY AND SECONDARY AEROSOLS

Friedlander (1973) is a brilliant synthesis, managed to resolve the primary and secondary components of a group of samples collected in the Los Angeles area. He estimated that roughly 40 percent of the total mass was secondary, with organic photochemical aerosol comprising roughly 24 percent. Other secondary materials were thus approximately 15 percent, predominately sulfates. Dams, et al. (1975) carried out an exhaustive analysis of a single large sample of particulate matter from Milan, Italy. They attempted no interpretation, but the data are sufficiently complete to permit some rough calculations. If it is assumed that the secondary organic material has the same elementary composition as assumed by Friedlander, and that all of the hydrogen in the sample is contained in the secondary organics, then such materials make up somewhat in excess of 30 percent of the total, while the sum of sulfate and nitrate is roughly 10 percent. Recognizing that these are all upper limits, it can be said that the Milan sample probably does not differ seriously from the samples examined by Friedlander. Hence, if one assumes the experience of Los Angeles and Milan to be universal, it would appear that the suppression of secondary aerosol formation would decrease airborne particle loadings by nearly one-half.

On the other hand, Harrison, et al. (manuscript, source unknown) seemed able to account for a very large percentage of the total particulate matter collected in Chicago as primary particles. If the data of Lodge, et al. (1960) can be taken as even remotely representative, a large fraction of the organics in the Los Angeles air appear to contain contemporaneous carbon. It is to be anticipated that these would also be highly oxygenated species, and quite conceivably indistinguishable from smog aerosol by the mass balance technique employed by Friedlander. A similar argument can be applied to the Milanese data as well. These findings certainly do not invalidate the previous argument, but could open it to question until further data, based on size fractionated aerosols, can be adduced.

Now let us examine the data of Willeke, et al. (1974) for two sites in and near Denver, Colorado during the late Autumn. At a site slightly to the North of the City, in the middle of the drainage plume, with largely cloudy skies and a mean temperature over a period of almost a week of 9°C, they measured a mean concentration of the order of 400 micrograms per cubic meter, with nearly 90 percent of the particles being above one micrometer in size. At the same time, nearly 90 percent of the particle surfaces was in the range below one micrometer.

Considering the low insolation, the low temperature, the particle size distribution and the particle surface distribution, it is extremely unlikely that secondary aerosols played any role in this set of aerosol data. Interestingly enough, Sverdrup, et al. (1975) cite a similar set of data collected during a summer night near Fort Collins, Colorado in a very clean area. Although the numbers are far smaller, the relative size distribution is very similar. They comment that the mode at a size around 19 micrometers or larger was an invariable constituent of Colorado samples. It might be noted that, out of more than 60 particulate monitoring stations in the State of Colorado, no more than 12 appeared to meet the Federal Secondary Standards during 1973 (Colorado State Air Pollution Control Program, 1974). Uncompiled data from the particulate sampling network in Colorado strongly suggest that it is difficult consistently to meet the National Air Quality Standards in any community of greater than approximately 500 persons. There is in fact a reasonable indication that there are portions of Colorado with a population density of fewer than 10 persons per square mile in which the Federal Primary and/or Secondary Standards are frequently exceeded. (The previously cited work of Harrison and his colleagues in Chicago also showed soil materials to be a major component in the air of Chicago.)

STRATEGIES FOR DECREASING TOTAL PARTICULATE LOADINGS

Very evidently the foregoing data do not completely catalogue the variations possible among cities and, in fact, sites within cities. No attempt has been made to explore some fascinating deviations from the norm, such as a few periods of data from Whitby's group, both in Los Angeles and in Denver, when the normal relationships between visibility and particle loading broke down totally. There are also certainly other that could be adduced to prove miscellaneous other points. However, these cases appear to represent extremes, and thus to define the field within which control strategies must operate. Typical aerosol levels for Los Angeles are somewhat in excess of 100 micrograms per cubic meter. Hence a total control of all substances leading to secondary aerosol formation would presumably bring Los Angeles into compliance with the Federal Primary Standards, assuming that the days measured there are typical. Periods of measurement for Denver were unquestionably atypical; some photochemical pollution does occur during the summer-time. Nevertheless, they comprised a sufficiently long period to demonstrate that the air quality standards would be frequently exceeded in the total absence of secondary reactions. (It should be noted that sulfate and nitrate comprise something of the order of 3 percent and one percent, respectively, of the total Colorado aerosol, virtually independent of the part of the state in which the measurements are made.) (Colorado State Air Pollution Control Program, 1972). It is difficult to interpret these as secondary aerosols. It should also be noted that, if these compositions are fairly constant, there will be numerous days when the total sulfate content will exceed the limits delineated by the CHESS study of 10-15 micrograms per cubic meter sulfate as the threshold of physiological effect. Making the reasonable assumption that these species are contained in the large particle fraction, it may be necessary to use a size-discriminating collector to separate the effects of natural sulfate from the presumably toxic anthropogenic component.

Realistically, total control of substances forming secondary aerosols is as improbable as total control of any other pollutant. Even for the clearest case, the Los Angeles Basin, a practical degree of control would only marginally allow the area to meet the ambient standards. To the extent that the estimates of secondary aerosol comprise maximum values, this strategy would fall short. Control of primary particulate pollutants, on the other hand, controls the larger component even for Los Angeles. In addition, if the deductions of Goetz and Pueschel (1965) have any validity, control of primary pollutants would also result in a decrease in secondary pollutant deposition as well. Clearly a major effort at secondary pollutant control would have little effect on excessive particulate loadings during a major portion of the year in Denver. Contrasting these two cities, Los Angeles and Denver, it becomes clear, first, that the question of control of secondary particles is almost meaningless. There is good reason to control hydrocarbons and nitrogen oxides in Denver because photochemical smog, with high oxidant concentrations, occurs all too frequently during the summer months. Should a health effect of sulfates be demonstrated, there is good reason to control sulfur oxides, the undoubted cause of secondary sulfates. It should be noted that primary sulfates, where they exist, are not in the respirable size range and hence would be unlikely to cause health effects. With regard to Los Angeles, to the degree that these substances are controlled as a means of decreasing oxidant and sulfate concentrations, a more or less corresponding reduction in secondary aerosols can be expected. However, it is clearly necessary also to control the primary aerosols that make up, even in Los Angeles, more than half of the total mass, and that appear to be the nuclei on which the secondary aerosols form. In Denver, such control of primary aerosols is mandatory and central. Furthermore, since the primary mass is in the large size range, it appears that fugitive dust control could well accomplish more than further imposition on emitting industries.

POSSIBLE REVISION OF STANDARDS

The data base for possible standards revision appear Totally inadequate. The available epidemiological data are all based on total loadings without regard to size distribution. It will require a number of years of work, starting now, to test correlations of community health with particular portions of the total particle size distribution. While it seems rational to anticipate that the primary health effects will be associated with particles below one micrometer, this must (a) be demonstrated and (b) be connected with actual particle concentrations. Obviously, a particulate loading of, say, 100 micrograms per cubic meter, 90 percent of which is below one micrometer typical of Los Angeles, can headly be expected to compare with the same loading in Denver with 90 percent of the mass above one micrometer. Farther than this it is difficult to go. It is also necessary to weigh the esthetic/economic effect of such a high concentration of settlable particles as appears to be typical of the Denver area. Once again, however, inadequate data exist to turn this into a standard, since data of this sort have been measured predominately in cities with a moister climate, and therefore probably lower concentrations of large particles, although very possibly similar total airborne concentrations. The best summary that it is possible to give of the present situation is that there is probably inadequate evidence seriously to change the present standard. However, it should be recognized that this standard is itself a very shaky figure, and probably not of equal applicability in all places. Particular problems in meeting it will exist in the more arid portions of the country, yet the respirable fraction of the particles will be far smaller in such areas than in moister climates at the same total particle concentration. There also appears to be some basis for allowing the deletion of high particle concentrations that are coincidence with winds in excess of approximately 15 or 20 miles per hour.

NEEDED RESEARCH

Obviously, the primary need is to repeat the previous types of epidemiological studies using both improved gas analysis techniques and the determination of particle size distributions as well as total loadings. New standards are needed at the earliest possible date to permit a realistic assessment of the true hazard of particulate matter. In view of control cost, a major expenditure to solve this problem seems amply warranted. Simultaneously, far better elemental and chemical analyses must be made, including, as appropriate isotopic analysis, to identify the true major sources of particulate matter in a number of cities.

For the drier climates, control priority must be given to fugitive dust. Certainly unpaved parking lots can be paved or sprayed with dust control agents, and more care may be taken to minimize the area denuded of vegetation at building sites. However, these considerations are of little use where the source of dust is agricultural activities. There appears to be real merit in research on, and a revival of interest in, shelter belts and other means of controlling wind erosion. Wind tunnel studies and field experiments need to be supported. There really appears to be a basis to believe that Denver might solve some of its particulate pollution problem by planting more trees! Meanwhile, there should be no cessation of work on the specific toxic effects of individual pollutant species.

SUMMARY

This study has highlighted, although it has not been limited to, a comparison of particulate pollutant data from Los Angeles and Denver, which apparently constitute two fairly extreme cases with regard to their particulate pollution problems, although mass concentrations are not wildly different on the average. Slightly less than half of the Los Angeles aerosol appears to be secondary. During a significant fraction of the year, virtually all of Denver's particulate pollution is primary.

Study of these two cases leads to the rejection of simplistic approaches on a nationwide basis. No single strategy will solve the problems of either city. All gains are likely to be incremental, and the total deployment of all reasonable strategies could well fail to solve either problem completely.

There is acute need for a better definition of the real problem areas in terms of concentration in each of the major size ranges, and for more and better analytical data on the ultimate composition of the particles, especially as a function of particle size. From health considerations, a high particulate concentration in Denver is probably less deleterious than a similar concentration in Los Angeles. However, high concentrations are not esthetically pleasing in either city, and every possible means should be deployed to control the respective sources of pollution.

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REVIEW
OF
SUSPENDED PARTICULATE MATTER

JUNE 1975

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SUMMARY RECOMMENDATIONS AND CONCLUSIONS

Projections for the U.S.A. made in this review (Fig. 11) indicate that the suspended particulate mass concentration in the atmosphere owing to anthropogenic secondary sources is at present three times that due to anthropogenic primary sources. By the year 2000, the secondary source contribution to the ambient atmospheric aerosol will be four times that from primary sources. These projections assume no positive control of emissions of the secondary source gases and vapors.

Effective national control of suspended particulate matter requires control of secondary source gases and vapors. The toxicity associated currently with secondary source aerosols (sulfate particulate for example) reinforces this recommendation.

Projections for the U.S.A. made in this review (Fig. 6) indicate that the suspended particulate mass concentration in the atmosphere owing to anthropogenic primary sources will nearly double within the next thirty years. This is based on the critical assumption that the product, (efficiency of control) x (application of control), is constant.

An aid in formulation of more effective particulate control strategies would be a systematic program to classify the various urban regions of the U.S.A. as to the relative contributions of primary and secondary particulate sources for each area.

Future particulate control strategies must be based at a minimum on knowledge of particle size and composition distributions of the ambient aerosol.

The research program of the atmospheric aerosol research section, Chemistry and Physics laboratory, National Environmental Research Center, Environmental Protection Agency has, over the past five years, greatly expanded our knowledge of the characteristics and dynamics of the urban aerosol.

Research into secondary aerosol formation should receive high priority. Current knowledge is inadequate of the mechanisms and rates of conversion of gases and vapors to aerosol.

Determination of the composition distributions of the major anthropogenic primary particulate sources should be assigned high priority. Insufficient information on these composition distributions is available at present.

Application of microscopy and source coefficient calculations for tracing ambient particulate matter back to sources appears to be feasible for the larger particles ($\gtrsim 2\mu m$). More knowledge of atmospheric aerosol dynamics appears to be necessary to identify finer particles with specific sources, owning to pronounced physicochemical alterations experienced by these particles in the atmosphere.

BACKGROUND AND INTRODUCTION

Under the provisions of the Clean Air Act we are not past the deadline for the status to protect public health by achieving required reductions in the ambient concentrations of the six major air pollutants. Yet, with the deadline just past, it is estimated that 75% of the population of the United States are still experiencing levels of suspended particulate matter and sulfur dioxide above ceilings established by the U.S. Environmental Protection Agency as requisite to protect the public health. It is clear that the air pollution control strategies formulated to date have not been successful.

This review looks at some of the deficiencies of current control strategies for suspended particulate matter and suggests alternatives together with forecasts of future trends.

Of the various air pollutants, particulate matter poses perhaps the greatest difficulty in the formulation of effective air pollution control strategies. From the outset, the term "suspended particulate matter" is almost hopelessly imprecise. In the atmospheric context, this term refers to an aerocolloidal suspension of particles of widely varying shapes, ranging in size from the molecular to the macroscopic and consisting of a bewildering variety of chemical species and physicochemical states. At the same time these particles in the atmosphere are participants in kinetic processes involving interactions between themselves, various reactive trace gases, and atmospheric dynamical processes.

While a control strategy may be proposed for particulate matter which parallels those for the various gaseous air pollutants, it is clear that, owing to the complexities noted, a true parallel does not exist and such a strategy is almost certain to be seriously flawed.

It is the purpose of this review to present an analysis of the complexities of atmospheric particulate matter and to indicate difficulties with current control strategies. Areas in which additional research is essential will be identified and suggestions will be given for future approaches to particulate control.

Particulate Regulation and Control

The incentive for control of suspended particulate matter stems from what are believed to be its adverse effects which arise at concentrations which presumably are above atmospheric "background". These include toxic effects arising from inhalation of particulate matter, reduced visibility, economic damage through soiling, corrosion and plant damage, and inadvertent weather and climate modification.

Of these adverse effects, particulate toxicity is the paramount concern and the current primary national ambient air quality standard for total suspended particulate matter for the U.S.A. (75 $\mu g/m^3$-- annual geometric mean; 260 $\mu g/m^3$--maximum 24 hr. concentration not to be exceeded more than once per year) is designed to protect the public health with an adequate margin of safety (1). The secondary standard (60 $\mu g/m^3$-- annual geometric mean; 150 $\mu g/m^3$--maximum 24 hr. concentration not to be exceeded more than once per year) specifies upper limits of suspended particulate matter requisite to protect the public welfare from any known or anticipated adverse effects (1).

To meet these specified ambient air concentration levels for total suspended particulate matter, individual states have promulgated emission standards which either are estimates of the effect that emission reductions might have on ambient particulate concentrations or are based on current technological and economic feasibility for reduction in particulate emissions from particular processes or sources. The notable feature is, of course, that the emissions controls are directed toward ensuring compliance with a given total mass concentration of ambient suspended particulate matter.

The present national primary air quality standard for suspended particulate matter represents then at best, a current estimate in relation to elimination of associated adverse health effects. This estimate has been arrived at principally through attempts at correlation of population morbidity and mortality data with total mass concentration of suspended particulate matter (or a measure thereof) together with, in some cases, sulfur or sulfate concentrations.

Of course, suspended particulate matter is a very imprecise term as has been noted above. The choice of total mass concentration as the index of the complex physicochemical system reflects in the main the historical circumstance that total mass concentration (or measure thereof) has been one of the indexes most conveniently measurable and was therefore the index most generally available when correlations with adverse effects were sought. Other parameters describing suspended particulate matter in the atmosphere are now becoming available on a routine basis and one can anticipate the alterations in control strategy will take place as a result.

Adverse Effects of Suspended Particulate Matter

As has been noted, many adverse effects have been traced to the presence of suspended particulate matter including increased morbidity and mortality rates, degradation of visibility, economic damage, and inadvertent weather and climate modification. Very little is known at present about the relation of suspended particulate matter to inadvertent weather and climate modification and such effects do not yet play an important role in shaping ambient air quality regulations. An exhaustive survey of the remaining adverse effects will not be presented, but a brief discussion will serve to indicate the importance of some of the important characteristics of suspended particulate matter.

Our knowledge of the inhalation risk from the urban aerosol or suspended particulate matter particularly in terms of long term, low level exposure is woefully inadequate. As Anderson (2) has pointed out, "The most important constituent currently measured in the air is dust, whether measured as suspended particulate, soiling index, or crudely (and less validly) as dustfall. It may be that dust per se seriously impars lung function, or that it is merely an integrated index of the presence of some as yet undetermined hazardous substance found in the ambient air". In fact, Amdur (3) has asserted that it would be toxicologically "astounding" if any of the effects observed in the laboratory or in ambient exposures could be causally related to an individual pollutant at observed ambient concentration levels. Thus, the safest conclusion is that adverse health effects probably arise as a result of highly complex interactions between suspended particulate matter, trace gases and concomitant meteorological phenomena.

Whatever the case, it seems clear that particulate health effects (ruling out of the discussion here deposition and subsequent absorption of particles from the body surface) must at the outset bear some relation to the probability of deposition of particles in the respiratory system, which is in turn dependent on the aerodynamic characteristics of the particles. Particles larger than a few micrometers are filtered from the incoming air in the nasel passage and in the remainder of the upper respiratory system. Particles in the size range 0.1 to 1 μm are deposited with the poorest efficiency and therefore are capable of deep penetration into the lung to the region the alveoli where clearance mechanisms are extremely inefficient. This dependence of deposition efficiency on particles size is summarized in Fig. 1 for particles of unit density (4). The deposition curves are modified for particles of different density, although for reasonable values of density the pronounced minimum in the range 0.1 - 1 μm remains.

The principal correlations of adverse health effects generally link particulate matter and sulfur oxides. Table 1 summarizes some of these correlative studies, upon which current regulations discussed above are based (5-11). A more recent review by Lave and Seskin (12) implicate particulate matter more definitely. The very recent reported results of the CHESS program (13) indicate that particulate sulfate may in some cases, be the principal determinant of adverse effects as indicated in Tables 3 and 4. Sulfate particulate is generally found in the submicrometer range where as indicated in Fig. 1 such particles penetrate deeply into the lung.

The CHESS and other more recent studies indicate that the composition of the particle may be the critical factor. Toxic effects of particulate matter, must, of course, be related to the interaction of deposited particles with material at the site of deposition. Possible effects produced by inhaled particulate matter after deposition are summarized in Table 5 (14) where particles are divided into the broad categories "soluble" and "insoluble" (in water). A primary example of a soluble toxicant would be sulfate particulate matter while asbestos represents a well recognized insoluble toxicant (whose toxic action, however, may possibly be linked to the slow solution of silica in the lung fluids).

Composition, then, also may be a critical factor in particulate health effects. Particulate components known to be systemic poisons, such as lead, mercury, beryllium, etc. should be, of course, subject to specific regulation as to their allowable concentrations. Only recently have comprehensive programs been initiated to identify the particulate organic and inorganic fractions in detail. This information together with a knowledge of the distribution of composition with particle size should prove to be invaluable in assessment of possible toxic effects.

It is clear that particle size and density play a primary role in determining the region of deposition in the lung. Once deposited, particle compositions should be essential in considerations of possible toxicity. Of course, other characteristics of particles may be of importance.

Particle morphology may be of importance in clearance efficiency of deposited particles from the lung; the morphology of asbestos is strongly implicated in asbestosis, for example (15). Particle shape, for example, is receiving increasing attention. The urban aerosol has been shown (16) to consist of a great variety of shapes classified into such generic shape categories as: spherical, crystalline, platelet, fibrous, amorphous, bulky agglomerate, and flat agglomerate.

There have been suggestions (17) that particulate matter may combine with trace gaseous compounds to produce synergistic effects. This view advances the hypothesis that particles may adsorb or absorb gaseous constituents and facilitate the transfer of these gases deep into the lung. According to this, then, the particulate specific surface area for adsorption, such as may be determined for example by the BET method, would be an important characteristic of the urban aerosol in relation to adverse health effects.

There are, of course, other parameters of suspended particulate matter which may eventually be relatable to possible health effects. These include such characteristics as electrical charge, radioactivity, chemical states (free radical density, for example), etc. One can only state that we have insufficient information at present to take us past speculation on possible roles of such characteristics.

That urban aerosol is the principal agent of degradation of urban visibility is generally accepted today (18). Furthermore, the mechanisms by which visibility is degraded are well understood in terms of characteristics of an aerosol particle.

The particles composing an aerosol decrease visibility by scattering and absorbing visible incident light. The total extinction, b_{ext} of light of wavelength λ by atmospheric aerosol may be calculated easily if one assumes that the particles are all spherical and of the same composition by the equation:

$$b_{ext} = \sum^{N} \pi r_i^2 Q_i n_i \qquad (2.1)$$

Where Q_i is the extinction efficiency of a particle of size class i and is a function of the parameter $2\pi r_i/\lambda$ and the refractive index, m, of the particles. n_i is the number concentration of particles of that size class, there being N such size classes accounted. r_1 is the particle radius.

Equation (2.1) serves to suggest the various characteristics of atmospheric aerosols which have to do with visibility. The number concentrations of particles in given size classes (in other words, the size distribution) is clearly of importance. Since Q_i is a function of refractive index which is in turn a characteristic of the chemical nature of the particles, particle composition is of importance. As we shall see, particle composition (as for example the water soluble components) may also play a role in determining the n_i and m for the atmospheric aerosol.

The relation of total light scattering to particle size and refractive index is indicated in Fig. 2 (19) where K_s, the total scattering coefficient ($Q_i = K_s + K_{abs}$, K_{abs} the total absorption coefficient), is presented as a function of particle radius, r, at various values of the real part of the particulate refractive index. The notable feature of Fig. 2 is the occurrence of large modes in K_s in the region of visible light at values of particle radius in the range 0.1 - 0.5 μm for a wide range of refractive index. That is, particles of radius near the wavelength of visible light scatter that light with greatest efficiency. This fact coupled with the universal observation that particles in this same size range are very numerous in the atmosphere as shown in Fig. 3 (20), means that most of the light scattering in the atmosphere is due to particles in the size range 0.1 - 1.0 μm. The few measurements available at present tend to indicate that the contribution of absorption to total extinction is small. Fig. 4 (21) exhibits explicitly for the Los Angeles aerosol the overwhelming dominance of the size range 0.1 - 1.0 μm to light scattering and hence degradation of visibility in this case.

Of course, as has already been remarked, atmospheric aerosols are of varied shape, not all spherical as suggested by equation (2.1), and may have widely differing chemical composition (and hence refractive index) within and between size classes. Thus, even though the physics of light scattering by particles is well understood, it is not simple to propose a detailed model for degradation of visibility due to the atmospheric aerosol. A field observation such as indicated by Fig. 4 serves to suggest that calculations based on the concept of particles as spherical and of a given refractive index do not seem to give rise to results out of line with expectations. The uncertainties regarding degradation of visibility seem with present knowledge, therefore, to reflect merely the general uncertainty in the factors which determine n_i the size distribution of the atmospheric aerosol.

Several studies, e.g. (22, 23) have focussed on the economic loss (in addition to that from adverse health affects) resulting from particulate matter. Specific categories of loss have been identified including corrosion and degradation of materials, damage to vegetation and lowered property values. Most of the studies in this category have dealt with correlations between some gross index of suspended particulate matter and the particular category of damage.

The relation of specific characteristics of the urban aerosol to economic loss has not been fully explored. There is, of course, the obvious relation of degraded visibility to general perception by a population of air pollution with consequent lowering of property values. Damage to materials and vegetation from particulate matter must entail as a first step, particle deposition followed by chemical and/or physical interaction. Hence, particle size and composition are both important characteristics in relation to the potential for economic loss due to particulate matter.

Processes and Characteristics of the Urban Aerosol

As the cursory review of adverse particulate effects has indicated, various characteristics of the urban aerosol must be central in the formulation of effective control regulations. These characteristics may be summariced:

(1) Particle size distribution
(2) Particle composition distribution
(3) Particle specific surface area distribution
(4) Particle shape
(5) Particle electrical charge distribution
(6) Particle radioactivity distribution

For the urban aerosol, these various characteristics are the result of a number of complex processes occurring in the atmosphere. These are indicated schematically in Fig. 5 which indicates also the relation of the size and composition distribution (the remaining characteristics are implied) to the adverse effects which in turn, are the basis for ambient air quality regulations.

As indicated in Fig. 5, particle size and composition distributions in urban atmospheres arise as a result of generation processes, growth processes, and removal processes. Aerosols are generated in urban atmospheres through injection from primary sources, which are those sources which introduce particles directly into the atmosphere, and creation by secondary sources which are associated with atmospheric chemical reactions between various trace gases. Particles in the atmosphere may undergo various growth processes such as coagulation or agglomeration and condensation or accretion. Finally, particles are removed from the urban atmosphere by several processes including advection, convection, dispersion, scavenging by hydrometeors and water clouds and dry deposition (particles removed at the earth's surface in the absence of primary and secondary sources are generating suspended particulate matter in the atmosphere where the various physico-chemical growth and removal processes act to produce finally an urban aerosol with certain size, composition specific surface area, etc. distributions.

Of course, no feasible methods have ever been proposed to regulate and control the natural processes of particle growth and removal. Therefore, as indicated in Fig. 5, ambient air quality regulations must be achieved through control of the primary and secondary sources of urban aerosols - that is, by reducing the emissions of particulate matter and trace gaseous species.

3. Primary Sources

For the continental tropospheric aerosol a rough estimate (24) attributes 50 to 60% of the total aerosol mass to primary sources. These are the sources which inject particles directly into the atmosphere. Current control strategies are directed toward reduction of anthropogenic primary source emissions through imposition of control technology in the familiar forms of mechanical collectors, scrubbers, filters and electrostatic precipitators. An answer to the question of whether or not this strategy is cost effective requires a detailed understanding of the atmospheric aerosol growth processes and a detailed knowledge of the important characteristics of primary source aerosols.

This section examines the current state of knowledge of primary source emissions in terms of the particle size and composition distributions.

As shown in Table 6, on a world-wide basis, aerosol sources may be divided into the two general categories, primary and secondary. The secondary sources arise from formation of condensable species as a result of atmospheric chemical reactions between various gaseous species. One further distinguishes within these categories the anthropogeric and natural sources. This distinction for primary sources may be in some cases rather unclear. For example, dust rise by wind may be owing in some regions to certain agricultural operations or poor agricultural management. Dust rise by wind action is a natural process, but man may in some regions, as noted, increase this process by his actions. The extent of this increase is difficult to document so that the distinction between anthropogenic and natural primary sources in this instance is blurred.

In the U.S. much of our knowledge of anthropogenic primary sources stems from the use of emission factors which attributes, in the case of particulate matter, a certain mass emission from a given consumption or production in a process (25).

These anthropogenic primary source emissions are also conveniently divided into two categories, stationary and mobile sources.

Table 7 (26) presents the various categories of stationary primary sources together with projections of particulate emission levels calculated by use of the emission factor concept. The three different cases in each year correspond to:

(1) Net control of particulate emissions is assumed to be constant for each industry at the 1970 value.

(2) Application of control is increased to 100% over the IRS plant lifetime and efficiency of new controls is increased based on an estimated technological growth forecast. It anticipates regulatory activity over all stationary primary anthropogenic sources.

(3) Same as case (2) plus increasingly efficient emission standards.

A similar estimate may be made for mobile sources. The most important of these are highway vehicles which are projected to have a constant emission factor of 0.38 g/mi for exhaust particulate and 0.20 g/mi for tire wear particulate. For highway vehicles, one must also consider an emission factor for highway dust (27) arising from surface stresses from vehicular traffic on roads; the emission factor is dependent on vehicle speed and road surface and has not yet been simplified into a single factor by means of a generalized test cycle.

While the concept of emission factors has been a valuable method in the past, it is now widely recognized to be too inaccurate for formulation of the more exacting strategies now recognized as necessary to meet ambient air quality standards. The source coefficient method, to be discussed below, offers the possibility of an important advance in knowledge of the contribution of primary sources to the ambient aerosol at a receptor point. Unfortunately, at present, this method is likely to be as inaccurate as estimates based on emission factors.

Particle size distribution

In terms of meeting current ambient air quality regulations for particulate matter, the particle size distribution of aerosol from anthropogenic primary sources is perhaps the most important factor. This aerosol characteristic is the determinant of particle residence time in the atmosphere and hence of the mass of suspended particulate due to a given primary source.

It is of consequence, therefore, to investigate the nature of possible processes generating particles from primary sources. Particles from a given primary source may be generated by the processes of nucleation, comminution, or by combinations of these processes.

Nucleation may be homogeneous or heterogeneous. The term homogeneous nucleation embodies all those processes in which vapour molecules interact physically or chemically to form particles; the particle growth process begins from particle sizes of molecular order and may proceed by coagulation, condensation or a combination of these. In heterogeneous nucleation, new particles are not formed; vapour molecules condense physically or chemically onto existing particles, and, primary, one is dealing with a condensational growth process.

Particle generation by comminution involves successive, usually mechanical, subdivisions of liquids or solids to the fine particle state. Aerosol generation at the air-sea interface and dust rise by wind action at the air-land interface are important examples of natural primary sources of particles formed by comminution. These sources, in fact, are estimated (24) to constitute the two largest contributors of aerosol mass on a world wide basis.

With these definitions, characteristics of the particle size distribution produced by the particle generation processes of nucleation and comminution will now be examined.

Homogeneous nucleation

Automobile exhaust represents perhaps one of the important examples of an anthropogenic primary source in which particles are apparently generated principally by homogeneous nucleation as defined here. The residence time of the aerosol, before injection and subsequent fairly rapid dilution in the atmosphere, in this and other important industrial combustion sources, is usually of the order 0.1 ~ 1 s. Therefore, the particulate emissions from such sources, are comparatively well-aged aerosols, for which the particle size distribution has had sufficient time to reach a "self-preserving" form by coagulation (30). The term "self-preserving" refers to the tendency of aerosols coagulating with the same collision parameter, b (μ,μ'), to achieve similar particle size distributions after succifient time of coagulation. Also, a simple calculation is sufficient to show that usually aerosols formed by homogeneous nucleation will, in the time period 0.1 ~1s, have an average size which is the submicrometre range. If M is the total mass concentration of condensed material formed by nucleation, the order of the mean radius of the coagulated aerosol should be:

$$r \sim \left[3M(1 + bN_o t)/4\pi\rho N_o\right]^{1/3} \tag{3.1}$$

where N_o is the initial embryo concentration and ρ is the particle density.

Eqn. (3.1) becomes for $N_o t \gg 1$:

$$r \sim (3Mbt/4\pi\rho)^{1/3} \tag{3.2}$$

and the order of the mean radius becomes independent of N_o. As an example, for an automobile using leaded gasoline, the undiluted exhaust has a total particulate mass concentration, M, of 10^{-7} -10^{-8} g/cm^3. Eqn. (3.2) indicates, as do measurements, (31) that most of the aerosol is certainly in the submicrometer range.

For anthropogenic primary sources of aerosol formed principally by homogeneous nucleation and in which subsequent particulate growth is by coagulation, one might infer that particle size distributions from all such sources are of the "self-preserving" form. The inference is the same if simultaneous condensation occurs (32).

Published studies (30) of the numerical solution of the coagulation equation in the free molecule and continuum regimes support the foregoing conclusion. However, experimental measurements of coagulating aerosols reveal that generally the aerosol is more polydisperse than predicted by the self-preserving functional form. The explanation for this behavior is a very familiar one to statisticians (32). The aerosol measured in the coagulation experiments does not represent a single population, but instead a mixture usually in random proportion of a heterogeneous population.

In other words, the aerosol actually measured is a composite of many different aerosol populations, each with a different history. Thus, the particle distribution function realized in an experiment, G(X) is:

$$G(X) = \sum_{i} \rho_i F_i(X) \qquad (3.3)$$

where the ρ_i are random weights attached to the various members of the heterogeneous population each with distribution functions $F_i(X)$.

For an infinitely composite population:

$$G(X) = \int F(X,a) dU(a). \qquad (3.4)$$

In an experimental realization of coagulation, not only systematic spatial or time variations or random experimentar error serve to create a composite population but, for dilute systems, unavoidable random fluctuations also contribute.

As a result of the effect of heterogeneity of population, the aerosol formed by homogeneous nucleation from a given primary source will always be more polydisperse than predicted by the increase in polydispersity for a given primary source will probably depend on the details of that source such as geometry, flow dynamics, etc. As a result, it remains to be determined whether or not for various primary sources of this type generalizations are possible. Certainly the fact of the "self-preserving" form provides a useful base from which to proceed in the inquiry.

Heterogeneous nucleation

The dense hygroscopie plumes emitted from various industrial processes are examples of aerosols formed by heterogeneous nucleation. In these instances, water vapor has condensed on an existing hygroscopic aerosol, which may itself in turn have been generated by homogeneous nucleation or comminution.

Without consideration of the complex initiation process, for the simple process of condensation of a pure substance on an aerosol of some given initial density function $n_0(r)dr$ of particle radius, r, it is a simple matter to examine the development in time of $n(r,t)$. In this case the volution of $n(r,t)$ is:

$$\frac{\partial n}{\partial t} + \frac{\partial}{\partial r} f(r)n = 0 \tag{3.5}$$

where $f(r)$ is the growth law for a particle of radius r. For example, in the continuum region $Kn \to 0$, neglecting the Kelvin effect, $f(r) = a/r$, where a is a constant (33). Similarly, in the free molecule region, $f(r) = a'$, a constant (33), if the Kelvin effect is neglected.

Eqn. (3.5) is a first order equation for which solutions may readily be found for arbitrary initial conditions. However, perhaps the most interesting feature of the pure condensation process is the tendency of condensation to produce a less polydisperse aerosol in the continuous region, when the Kelvin effect can be neglected. In this case, it is a simple matter to show the ratio of the standard deviation σ to the mean radius γ_1, approaches zero with increasing time:

$$\frac{\sigma}{\gamma_1} = \frac{\sigma_0}{(\gamma_{1,0} + 2at)^{\frac{1}{2}}} \tag{3.6}$$

where the subscript $_0$ designates initial conditions.

Similarly, in the free molecule regine:

$$\frac{\sigma}{\gamma_1} = \frac{\sigma_0}{\gamma_{1,0} + a'N_0t'} \tag{3.7}$$

N_o being the initial total particle concentration. This characteristic of pure condensational growth has been utilized for the production of approximately monodisperse aerosols in variations of the original Sinclair-La Mer aerosol generator (33).

If, as in the previous examples, the concentration of condensing vapor is held fixed by the Kelvin effect is included in the term f(r), it can be shown that $\sigma/\gamma_1 \to 0$ as a result of condensation. However, if the quantity of condensing vapor is limited, one finds that in an initially polydisperse aerosol after condensation has proceeded, the smaller particles will begin to evaporate while the larger ones continue to grow.

Also, additional complication beyond the scope of this discussion arises in consideration of a hygroscopic aerosol which grows at humidities below the critical supersaturation of some of the particles. In such cases, n(r) can become bimodal and very polydisperse.

More general condensation processes, including stochastic effects, have been examined elsewhere (34). Such processes, as well as randomization indicated in eqn (3.3) and (3.4), usually act to increase the polydispersity of an aerosol. Additional complication can be introduced by considering as well simultaneous coagulation and condensation.

When the deterministic condensational growth described by eqn. (3.5) is the only process altering the aerosol size distribution, the final distribution clearly will be determined by the initial size distribution. This initial size distribution will be that owing either to homogeneous nucleation or comminution or both. When the condensation process is stochastic and/or randomization occurs, the final particle size distribution resulting from condensational growth will become asymptotically independent of the initial distribution, the equivalent of the "slef-preserving" behavior for a coagulating aerosol.

However, in general, it is much more difficult to draw conclusions concerning the nature of the particle size distribution resulting from condensation in these cases than for coagulation. Unlike the coagulation equation, the condensational growth equation is coupled to the conservation equation of the condensing vapor; the state of the suspending gas usually plays a secondary role in the coagulation of fine particles. Furthermore, the ability of particles to grow by condensation depends in detail on particle composition or surface properties; such characteristics are usually not considered to be of great importance in coagulation. Therefore, for sources in which particle generation by heterogeneous nucleation plays an important role, detailed examination of the process dynamics will be necessary to characterize the particle size distribution.

Comminution

Important natural sources of aerosol particles generated by comminution have been cited at the beginning of this section. Anthropogenic sources of aerosol generated by comminution are also of common occurrence and include emissions from industrial operations such as mineral, rock and gravel processing, sand blasting, cement manufacture, etc., as well as inadvertent emissions resulting from farming operations, etc.

The process of comminution begins with a body of macroscopic size and by successive subdivisions or splittings, liquid or solid particles capable of aerosolization are formed. It is therefore the inverse operation to homogeneous nucleation and subsequent coagulation. The evolution for comminution may be represented by the relation:

$$\frac{\partial n(\mu)}{\partial t} = \int_{\mu}^{\infty} c(\mu/\mu')n(\mu')d\mu' - c(\mu)n(\mu) \qquad (3.8)$$

where $c\ (\mu/\mu')\ dt$ is the probability that a particle of mass μ' will split in time dt to form 1,2,3... particles of mass μ and $c\ (\mu)\ dt$ is the probability that in the same time a particle of mass undergoes splitting. The basic assumption of eqn. (3.8) is that each particle splits with a probability independent of the presence of other particles. Clearly additional detail can be introduced.

It is possible to show that the splitting process approaches asymptotically a limit distribution (35) which, for certain assumptions concerning the splitting probabilities, can be approximated by the log normal distribution. Just as the coagulation process has for certain assumptions concerning collisions as asymptotic limit distribution, so too does the process of comminution.

A common assumption in the discussion of the splitting process (35) is that the probability of splitting is proportional to some power of the mass of a particle. Clearly, if a comminution process is carried out so that a particle of, say 1000 μm is split with unit probability, a particle of 1 μm radius will be split with a probability orders of magnitude less (10^{-9} in fact, if splitting is directly proportional to particle mass for particles of unit density). For this reason, many large sources of particles produced by comminution, such as those cited above, will produce particles in the range of larger particle sizes.

Although asymptotic limit distributions may exist for a given comminution process, randomization can be expected to be important, owing to the comparatively small number of particles per unit volume in typical comminution processes. However, very large particles are not important in the consideration of sources of air pollution, so that the distribution produced by a comminution process can be truncated at the order of 100 μm radius. Therefore, the particle size variation of interest will generally be over only one or two orders of magnitude of particle radius. As a result the range of polydispersity which might arise from randomization is restricted.

While this theoretical discussion may provide some qualitative insight into the particle size distributions from primary sources, mechanisms of particle formation in many primary sources are too complex for the simple generalizations suggested above to be of practical use. Hence, one must measure experimentally particle size distributions from particular primary sources. Even here, of course, generalization may not be possible. In any event, we do not know. Only limited studies have been published on the particle size distribution from primary sources (36, 37). At the present time there is indication (38) that more extensive experimental investigations are under way of particle size distributions from primary sources. It is suggested that any such experimental program should be sufficiently extensive that useful generalizations, even if a statistical nature, may be possible.

Particle composition distributions

As noted earlier, particle composition distributions provide critical information in regard to assessment of adverse effects of suspended particulate matter. While much information is being accumulated on the composition distribution of ambient aerosol, very little is known at present about the composition distribution of anthropogenic primary sources.

Some first steps have been taken to identify trace elements with certain primary sources (29,39). The variations of trace elements with particle size has been studied for fly ash from coal field power plants (40,41,42).

Table 8 (39) gives estimates of composition of emissions from some Chicago primary sources. Overall estimates such as these for various trace elem-nts form the basis for the method of source coefficients for tracing these elements in the ambient aerosol back to their sources. The technique is straight forward. Essentially, if P_i is the percentage of any element i in the aerosol (which is to be measured experimentally) then

$$P_i = \sum_j \alpha_{ij} P_{ij} C_j \qquad (3.9)$$

where p_{ii} is the percentage of element i in the particulate matter emitted from source j, C_j is the fraction of the aerosol sample contributed by source j, and α_{ii} is a coefficient allowing for changes in the proportion of that element which may take place as a result of various atmospheric processes. The source coefficient C_j is to be calculated from eqn (3.9) given knowledge of P_i and the α_{ii}, p_{ii}, which is, of course, precisely where there are the largest gaps in our current knowledge.

It is strongly recommended that studies be carried out of the composition distributions from primary sources and of the atmospheric processes which may alter the relative amounts of the various elements in the aerosol.

An additional promising method for tracing aerosol back to the primary source is now under active development. This method employs optical and electron microscopy together with electron and x-ray microanalysis to attempt identification of particulate samples collected on filters and impaction stages (43, 44, 45, 47, 48). For large particles, amenable to optical microscopy, direct identification of some types of particles appears to be possible from particle morphology and properties. Rubber tire dust, mica, quartz, cornstarch, paper fibers, plant parts, fly ash, coal fragments, limestone, etc. have all been identified as constituents of the urban aerosol and are traceable back to their particular sources. For smaller particles which must be examined by electron microscopy, x-ray microanalysis coupled with microscopy has aided in identification of specific fine particles such as automobile exhaust aerosol particles. For larger particles, the use of microscopy appears to be a feasible technique for identification of specific types of particles arising from particular primary sources. For sub-micron particles, however, in active chemical environments, there is sufficient mixing due to chemical reactions and accretion that this technique may have limited value.

Projections of atmospheric contributions from various anthropogenic primary sources.

Up to the present time controls on emissions of particulate matter from sources have been directed primarily toward reduction of total mass emissions. From a regional or international standpoint this may not be sufficient. Consider that the rate of change of total suspended particulate mass, m, owing to a primary source emission is a function of the primary source emission rate, a, and the residence time, b^{-1}, of the aerosols from that source. As is well known, these simple assumptions are not generally correct, but they are useful for this rough estimate.

The functional relationship described above may be expressed in the form:

$$\frac{dm}{dt} = a-bm \qquad (3.10)$$

where b^{-1} is a function of particle size, which for a particular source category will be chosen as the residence time of the mass median diameter. For short time periods:

$$\frac{dm}{dt} \sim 0 = a-bm \qquad (3.11)$$

so that $m = a/b$ gives the total mass of atmospheric aerosol at any time owing to a particular source category. Table 9 presents some comparisons for anthropogenic primary source categories in the U.S.A. In these examples, the largest tonnage sources of particulate emissions are not necessarily the largest contributors to the inventory of suspended particulate matter.

The data of Table 9 from Ref. (26) represent the assumption that net control of primary particulate emissions is assumed to be constant for each industry at the 1970 value through the year 2000. Production capacity will vary, but the product (efficiency of control) X (Application of control) is constant. The estimates of particle residence time as a function of particle diameter in Table 9 are owing to Esmen and Corn (64). These investigators attempted to establish these values through a series of indirect field measurements and their accuracy is difficult to assess.

It is notable that some of the largest source emissions in Table 9 (Rock Crushing, for example) are among the smallest contributors to the ambient aerosol mass. In fact, even if perfect control of the large particle sources were achieved, it would have little impact on the ambient aerosol mass, according to these estimates.

A further comparison is possible from the data of Table 9. If it is assumed that the diurnal average mixing height for the contiguous continental U.S. is 3000 feet, one may calculate from these data the average ambient aerosol concentration for the contiguous continental U.S. The results of this admittedly very crude estimation are displayed in Fig. 6 along with the total U.S. anthropogenic primary source emissions. It must be noted that the average ambient aerosol concentration calculated is only that part of the aerosol concentration due to anthropogenic primary sources. It does not include natural primary sources or anthropogenic and natural secondary sources. The calculation for Fig. 6 represents certainly an overestimation inasmuch as it does not allow for advection out of the contiguous continental U.S. nor does it allow for convective transport into the upper troposphere. Nevertheless, regarded as an average for the entire continguous continental U.S., the figures do not appear to be entirely unreasonable.

As seen in Fig. 6, the rate of increase of the average ambient aerosol concentration is larger than that of the primary source emissions themselves. This is owing to the relatively large residence time of the fine combustion particles from power generation and transportation sources which show considerable increases over the period 1970-2000. If lead is removed from gasoline, of course, the rates of increase shown will not be as large as has been indicated.

According to Fig. 6, by the year 2000 the average ambient aerosol concentration due to anthropogenic primary sources will be in excess of 80 ug/m^3, almost double the value of 1970. Of course, this represents an average for the U.S. and some areas would have much smaller and others much larger concentrations. If one adds in the natural background particulate concentration of 20-40 ug/m^3(51), and further adds in a value for secondary aerosol production (to be discussed in the next section) one would obtain values of 180-200 ug/m^3 for 1970 and of the order of 400 ug/m^3 for the year 2000. These large values result from the very large secondary source contributions as estimated in the next section.

4. Secondary Sources

The naive view of the atmospheric aerosol supposes that if one knows the size and composition distributions of particulate matter emitted by primary sources then the ambient aerosol is readily comprehended through consideration of the mixing and coagulation of these primary emissions together with alterations resulting from dispersion, advection and convection. That such is not the case has been known now for some time (20).

Subsequent to their injection into the atmosphere, primary source aerosols may be subject to a large number of alterations produced by various physicochemical processes including photochemical and thermochemical reactions. When they occur, these processes lead to growth of and substantial alteration of the chemical composition of the ambient aerosol. In those circumstances, without current incomplete knowledge, attempts to trace the ambient aerosol back to primary sources through use of the source coefficient concept are fraught with difficulties.

At present, in the U.S. the Atmospheric Aerosol Research Section of the Chemistry and Physics Laboratory, National Environmental Research Center, Research Triangle Park, Environmental Protection Agency has underway and is sponsoring effective research programs to determine the atmospheric aerosol growth processes, including secondary sources. To date, these efforts have been most fruitful and over the past five years our knowledge of the urban aerosol has been enormously enhanced. It is strongly recommended that this type of effort be continued and increased, particularly in the area of aerosol chemistry which comprises knowledge of secondary sources and aerosol growth processes.

This section reviews current knowledge of those atmospheric transformations leading to production of aerosol from gaseous chemical species. Sources of secondary aerosol are summarized. Resultant size and composition distributions are discussed. Finally, some projections are made for the ambient aerosol.

Sources of secondary aerosol

Many gases and vapors are known to enter into homogeneous chemical reactions which give rise to products capable of forming relatively involatile species and hence (under special conditions) condensation aerosol under tropospheric conditions.

In the urban atmosphere, homogeneous nucleation is believed not to occur if the aerosol surface concentration is higher than approximately 500 um /cc (63) At high surface concentrations heterogeneous nucleation instead occurs. One possible exception to this could be found in the nucleation of sulfuric acid aerosol:

$$SO_2 + \frac{1}{2}O_2 \xrightarrow{\text{Free radicals}} SO_3$$

which may interact rapidly with ambient water vapor:

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

$$H_2SO_4 + H_2O \longrightarrow H_2SO_4 \cdot H_2O$$

$$\vdots$$

$$H_2SO_4 \cdot nH_2O + H_2O \longrightarrow H_2SO_4 \cdot (n+1)H_2O$$

$$H_2SO_4 + H_2SO_4 \longrightarrow 2H_2SO_4$$

$$\vdots$$

$$mH_2SO_4 + H_2SO_4 \cdot nH_2O \longrightarrow (m+1)H_2SO_4 \cdot nH_2O$$

to form an aerosol by homogeneous nucleation. In more general case, relatively involatile products of homogeneous gas phase chemical reactions will condense onto the ambient aerosol (49).

Examples of reactions of possible importance in production of substances promoting growth of atmospheric aerosol by condensation are summarized in Table 10.

In addition, various trace gases and vapors are believed to enter into heterogeneous chemical reactions involving ambient aerosol. Details of these reactions have been studied in only a few cases such as in the oxidation reactions of SO_2 in aqueous solution aerosols. However, for many of the observed growth processes of suspended particulate matter, the details are as yet unknown. Table 11 lists some of the heterogeneous reactions which are believed to contribute to oxidation of atmospheric SO_2 and hence to aerosol growth.

The sorption of water vapor (the most abundant of the trace atmospheric gases and vapors) by the water soluble components of the atmospheric aerosol constitutes an interaction of very special importance. This process is associated with a large part of the visibility reduction from the soluble fractions of the atmospheric aerosol and, of course, plays the central role in the formation of clouds.

It is possible that combustion and other energetic processes may inject into the atmosphere vapors of relatively involatile substances which may subsequently condense (physically) onto the ambient aerosol. This has not been studied, evidently. However, it would be expected that such processes would provide only minor contributions to the total aerosol mass.

The condensation onto the ambient aerosol of atmospheric small ions and radioactive species (such as the radon daughters) plays a very special role in air pollution and toxicology (54, 55) but again, is not believed to be of central importance in the evolution of the atmospheric aerosol.

Much work remains to be done to elucidate the various mecahnisms leading to formation of secondary aerosol. It must not be supposed that current knowledge is adequate. Particularly complex are the formation and atmospheric transformations of various organic vapors to the particulate phase. It appears that in photochemically active environments organic gases and vapors may be the principal source of secondary aerosol (52). Yet, our knowledge of aerosol formation in this case is very sketchy in spite already of extensive smog chamber and atmospheric investigations (52). This subject should receive high priority in future research programming.

Secondary and primary urban aerosols

For the U.S. and for most cities it is very difficult to generalize concerning the relative importance of primary and secondary sources in particulate pollution. In a well documented case, we know that the Los Angeles aerosol may owe as much as 70 to 80% of its mass to secondary sources at some times (56). On the other hand, during winter pollution episodes in Denver, the aerosol appears to be almost entirely dominated by primary sources (52, 57).

Many factors may be responsible for dominance of secondary or primary sources. In the case of Los Angeles, climatological and meteorological conditions combine with strong sources of NO_x and organic compounds to produce an aerosol evidently dominated by secondary sources. In northern cities in winter time conditions, it is suggested here that the low ambient temperatures may ensure that the aerosol of these cities is dominated by primary sources. It has been shown that photochemical reactions and subsequent aerosol growth are reduced significantly at low temperatures (58-61). Other as yet unspecified conditions may cause some urban areas to be dominated by either primary or secondary aerosol sources. Again, there may be also a diurnal variation in addition to seasonal variations of secondary/primary sources.

In brief, based on current knowledge it is not possible to classify, except in some cases, major urban areas as dominated by primary or secondary sources at particular times. Means for arriving at such classifications should certainly be sought on a priority basis. Such knowledge is essential, as has been discussed, for formulation of rational particulate control strategies.

Aerosol size and composition distributions

As has already been noted, aerosols observed in the atmosphere appear to form and evolve by a complex combination of physico-chemical processes. These processes may involve chemical reactions of gaseous species, homogeneous and heterogeneous nucleation, condensation, coagulation, input of particles from primary sources, sedimentation and deposition processes, and various fluid dynamical phenomena such as convection, dispersion and mixing. The particle size distribution of an aerosol observed at a given time is the result of the competition between and the action of these various processes. Owing to the complex, non-linear nature of the operation of all these processes, it is clear that statistical correlations of field data will in general be inadequate for providing a basis for particulate control strategies or specific control decisions and that explicit knowledge of the dynamics of the processes shaping the particle size distribution is required.

Just as for investigations of complex homogeneous gas phase chemical reactions, detailed mathematical models have proven to be invaluable, so too far an understanding of aerosol dynamics in the atmosphere or in smog chambers are mathematical models useful. Whether or not such a program can succeed for complex atmospheric aerosols remains to be seen.

Complete knowledge of all processes shaping the particle size distribution implies also knowledge of the distribution of the innumerable chemical species making up the particles--that is, knowledge of the multivariate particle composition distribution: $n\ (x_1, x_2, x_3, \ldots x_n;\ r,\ t)$ which gives the number of particles at a point in space $\overset{>}{r}$ at time t having masses of chemical species 1, 2, 3..., m in the range x_1, dx_1 ; x_2, dx_2; ...; x_n, dx_n . $\sum_{i=1}^{n} x_i = s$.

The evolution of $n_n\ (x_1,\ x_2,\ x_3,\ \ldots\ldots\ldots,\ x_n\ \overset{>}{r}, t)$ in time is extremely complex and numerical simulation appears prohibitive at present. However, one does not require usually such complete information for the aerosol. In that which concerns some of the principal adverse effects of particulate matter, it is probably possible to follow the evolution of much less complex distributions. $n_2(y,\ z;\ \overset{>}{r},\ t)$. $n_2(y, z; \overset{>}{r}, t)$ is the distribution function for an aerosol composed of two classes of material, A and B, or alternatively, composed of two different chemical species, A and B. Thus $n_2(y, z;\ \overset{>}{r}, t)$ is the number of particles at r,t having masses of species A in the range y,dy and masses of species B in the range z,dz. A and B could be, for example, respectively the hygroscopic and non-hygroscopic components of an aerosol particle. This is an important division in practice for it is the amount of water soluble hygroscopic material in a particle which determines size of the particle at a given relative humdity. Also significant adverse health effects have been traced to the mass of sulfate in particular matter; sulfate of course would represent the important hygroscopic component of the particulate matter in an atmosphere rich in SO_2.

With certain assumptions (62), one can write down the conservation equations for $n_2(y,z;\vec{r},t)$ in the atmosphere as well as the conservation equations for those chemical species of mass concentration s_j participating in the growth processes of the particles. The evolution equations of this coupled system have the form:

$$
\begin{aligned}
\partial n_2(y,z;\vec{r},t)/\partial t + \nabla\cdot\vec{V}n_2 = {} & \nabla\cdot\bar{\bar{K}}\cdot\nabla n_2 \qquad (4\text{-}1)\\
& + \frac{1}{2}\int_0^y\int_0^z dy'dz'\, b(y-y',z-z',y',z')\, n_2(y-y',z-z')\, n_2(y',z')\\
& - n_2\int_0^\infty\int_0^\infty dy'dz'\, b(y,z,y',z')\, n(y',z')\\
& - \frac{\partial}{\partial y}[\psi_1 n_2] - \frac{\partial}{\partial z}[\psi_2 n_2] + \vec{G}\cdot\nabla n_2\\
& + \Sigma\dot{\nu}_p + \Sigma\dot{\nu}_N
\end{aligned}
$$

for the particulate phase. The left hand side of the equation represents the usual convective transport of n_2 in the atmosphere with mean velocity $\vec{V}$. The first term on the right hand side gives the dispersion of n_2 due to eddy diffusion where $\bar{\bar{K}}$ is the eddy diffusivity tensor. The second and third terms represent the change in n_2 owing to coagulation and the fourth and fifth terms the change due to deterministic condensation of trace gaseous substances The sixth term accounts for particle removal by gravitational settling where $\vec{G}(X)$ is the settling velocity of a particle of mass x. $\nu_p(y,z;\vec{r},t)$ of particles from primary source p with soluble and insoluble components. Similarly $\dot{\nu}_N$ $(y,z.\ \vec{r}t)$ is the rate of input of nuclei at $\vec{r}$,t from homogeneous nucleation processes N. Extensive discussions of the coagulation and condensation rate coefficients b and ψ can be found in several references (e.g. 33).

$$\partial s_j/\partial t + \nabla\cdot\vec{v}s_j = \nabla\cdot\bar{\bar{K}}\cdot\nabla s_j + \sum_p \dot{s}_{jp} + \sum_r \dot{s}_{jr} \qquad (4\text{-}2)$$
$$- \sum_{r'} \dot{s}_{jr'} - \int_0^\infty dy\, \psi_1 n_2 - \int_0^\infty dz\, \psi_2 n_2 - \int_0^\infty \int_0^\infty dy\, dz\, (y+z)\, \dot{\nu}_N$$

where s is the mass concentration of the j^th chemical species. The terms s_{jr} and s_{jr} represent respectively the rate of input and removal of j by chemical reactions r and r'. s_{jp} is the rate of input of j from primary source p. This set of equations should then detail the evolution in time of n_2.

If the particle growth processes are not dependent on the soluble fraction, one may then study the evolution in time of the particle size distribution n (x; $\vec{r}$,t). Detailed discussions of the derivation of the evolution of n has been given (62). The form of the coupled equations is analogous to that for n_2.

$$\partial n(x;\vec{r},t)/\partial t + \nabla\cdot\vec{v}n = \nabla\cdot\bar{\bar{K}}\cdot\nabla n + \frac{1}{2}\int_0^x dx'\, b(x-x',x')\, n(x-x')\, n(x') \qquad (4\text{-}3)$$
$$- n\int_0^\infty dx'\, b(x,x')\, n(x') - \frac{\partial}{\partial x}[\psi(x)n] + \vec{G}\cdot\nabla n + \sum_p \dot{\nu}_p + \sum \dot{\nu}_{Ni}$$

for the particulate phase, and

$$\partial s_j/\partial t + \nabla\cdot\vec{v}s_j = \nabla\cdot\bar{\bar{K}}\cdot\nabla s_j +$$
$$\sum_r \dot{s}_{jr} + \sum_p \dot{s}_{jp} - \sum_{r'} s_{jr'} \qquad (4\text{-}4)$$
$$- \int_0^\infty \psi_j(x)\, n\, dx \quad - \int_0^\infty \dot{\nu}_{Nj}\, x\, dx \quad , j = 1,2,\ldots$$

for the chemical species undergoing condensation.

Detailed analysis of the urban aerosol along the lines suggested above is, of course, a most difficult task. The description given here serves more as a framework for consideration of all relevant parameters which shape the urban particle size and composition distributions. Basic information on all the aerosol kinetic processes for various urban regions is now becoming available through the research programs of A.A.R.S., E.P.A.

In a few years the analysis suggested here should be possible in an approximate manner. Some first steps along these lines have already been taken (56,57), but much more remains to be done.

As a result of field studies undertaken since 1969 under sponsorship of A.A.R.S., E.P.A., a clearer, but still approximate picture of the particle size distribution of the urban aerosol has emerged. Figs. 7 and 8 reflect the current view (48) of the size distribution of the urban aerosol.

In this view, as indicated by Fig. 8, the mass distribution of the urban aerosol is a bimodal function of the particle diameter, reflecting, it is thought, the mixture of aerosols from the basic primary generation processes discussed above--that is, comminution and nucleation. One estimate (48) places approximately 1/3 of the total mass concentration of the urban aerosol in the size range below 2 μm diameter. There will be certainly considerable variation in this fraction as the complete aerosol dynamical situation is altered.

Figure 7 (48) indicates that the surface area size distribution may be trimodal near sources of combustion nuclei. Also this figure indicates schematically that this trimodal distribution is the result of the dynamical processes discussed in detail above.

The detailed picture of the processes shaping the urban particle size distributions are inferred by Figs. 7 and 8 will no doubt undergo modification as our knowledge of the urban aerosol becomes more fully developed. At present, the scheme given here seems to correspond well with our intuitive understanding of aerosol dynamics.

Fig. 9 (63) presents some results of partial composition distribution obtained by cascade impactor in Riverside, California. Shown, of course, is a partial distribution including sulfates, nitrates, lead, iron and total particle mass distribution. It may be noted that secondary aerosol, sulfates and nitrates, are predominantly found in particles smaller than 1 μm and that iron, associated with comminutive sources, is found in the particles larger than 1 μm.

Fig. 10 gives an example of particle size and composition distributions in photochemically active urban air. The indicated distributions correspond approximately with present limited knowledge (52). The particle composition distributions are not meant to be precise but indicate only possible ranges of relative abundance, according to the mass concentration, of the classifications water soluble/water insoluble and organic/inorganic. Water soluble organic species in the urban aerosol are believed to be concentrated in particle size below 1 μm. Water soluble inorganic species, as indicated in Fig. 9, tend to be found below 1 μm as sulfates, nitrates, etc. but in regions invaded by marine air, for example, the large particles may contain some sea salt constituents. Water soluble contributions to the larger particle mode may also be traced to soluble salts in soils or in dust from wintertime street and highway maintenance. Water insoluble organic species appear to be associated mainly with combustion and other high temperature processes, and therefore, they are found predominantly in the fine particles, particularly where particulate control technology is in effect. Water insoluble inorganic species are dominant constituents of the large particles from comminution sources.

Figure 11 presents the results of projections of the average U.S. ambient aerosol mass concentration due to secondary sources. It was assumed in this projection that secondary aerosol was distributed with a mass average diameter of 0.5 μm corresponding to in inverse residence time in the atmosphere of 27 yr^{-1} (64). Sources of secondary aerosol were identified as the oxidation reactions of SO_2, NO_x, reactive hydrocarbons, and NH_3 which yield particulate material. Projections of emission rates for these gases are from Hidy and Brock (65). It was assumed that 60% of the sulfur oxide emissions would be converted to aerosol, 40% of the nitrogen oxides, 30% of ammonia, and 2% of the reactive hydrocarbons. Of the total hydrocarbon emissions, 30% was assumed to be reactive.

There is no question that this type of projection rests on gross assumptions which will no doubt be refined as our knowledge of secondary aerosol increases. According to this projection, the anthropogenic ambient aerosol mass concentration due to secondary sources is now three times that due to primary sources. Owing in part to the assumption of better control of primary source emissions in the future (increased emissions of sulfur oxides owing to increased usage of coal is another factor), by the year 2000 the secondary source mass contributions will be nearly four times the primary source contribution.

These figures are overestimates for urban regions. The conversion rates of the trace gaseous species giving rise to aerosol are thought at present not to be too rapid, Hence, advection and convection tend to diminish greatly the importance of secondary contributions for most urban aerosols. However, on the average one would expect to see the average mass concentration over rural regions and over the oceans of the northern hemisphere rise as a result of the U.S. secondary aerosol contributions.

From this projection, it is discouraging to reflect that even if primary source emissions were completely eliminated, the nationwide average ambient mass concentration would only be reduced by 25-30%. Of course this is on a nation wide average. As noted above, many urban regions appear to have ambient aerosol dominated by primary aerosol in which case, of course, primary particulate control is very cost effective.

One can state safely that effective control of suspended particulate matter as a national policy requires control of secondary source gases and vapors. This view is considerably reinforced when possible health benefits arising from elimination of harmful aerosols is considered inasmuch as toxicity appears to be associated importantly with the secondary particulate sources.

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FIGURES

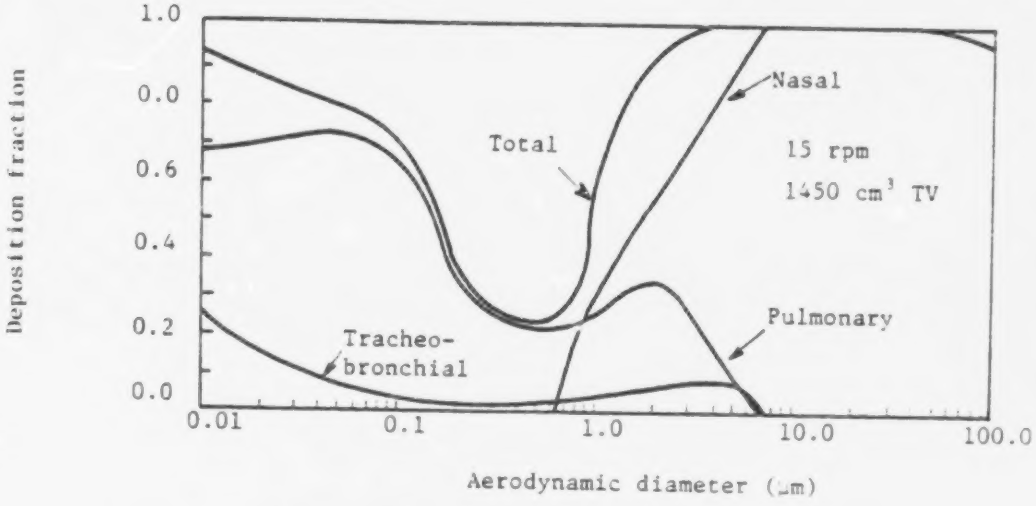

Figure 1. Deposition of monodisperse aerosols of various diameters in the respiratory tract of man (assuming a respiratory rate of 15 resyirations per minute and a tidal volume of 1450 cm^3). (4).

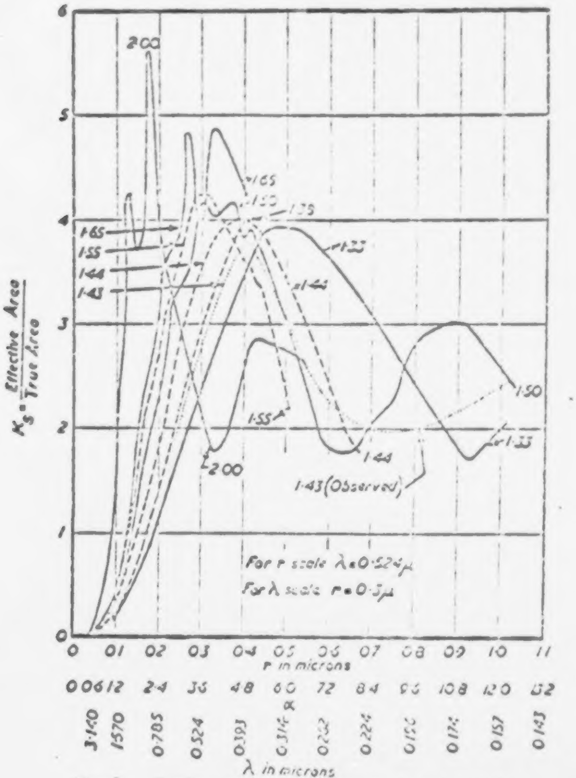

FIG. 2 Total scattering coefficient for spherical particles plotted against r, α and λ (19)

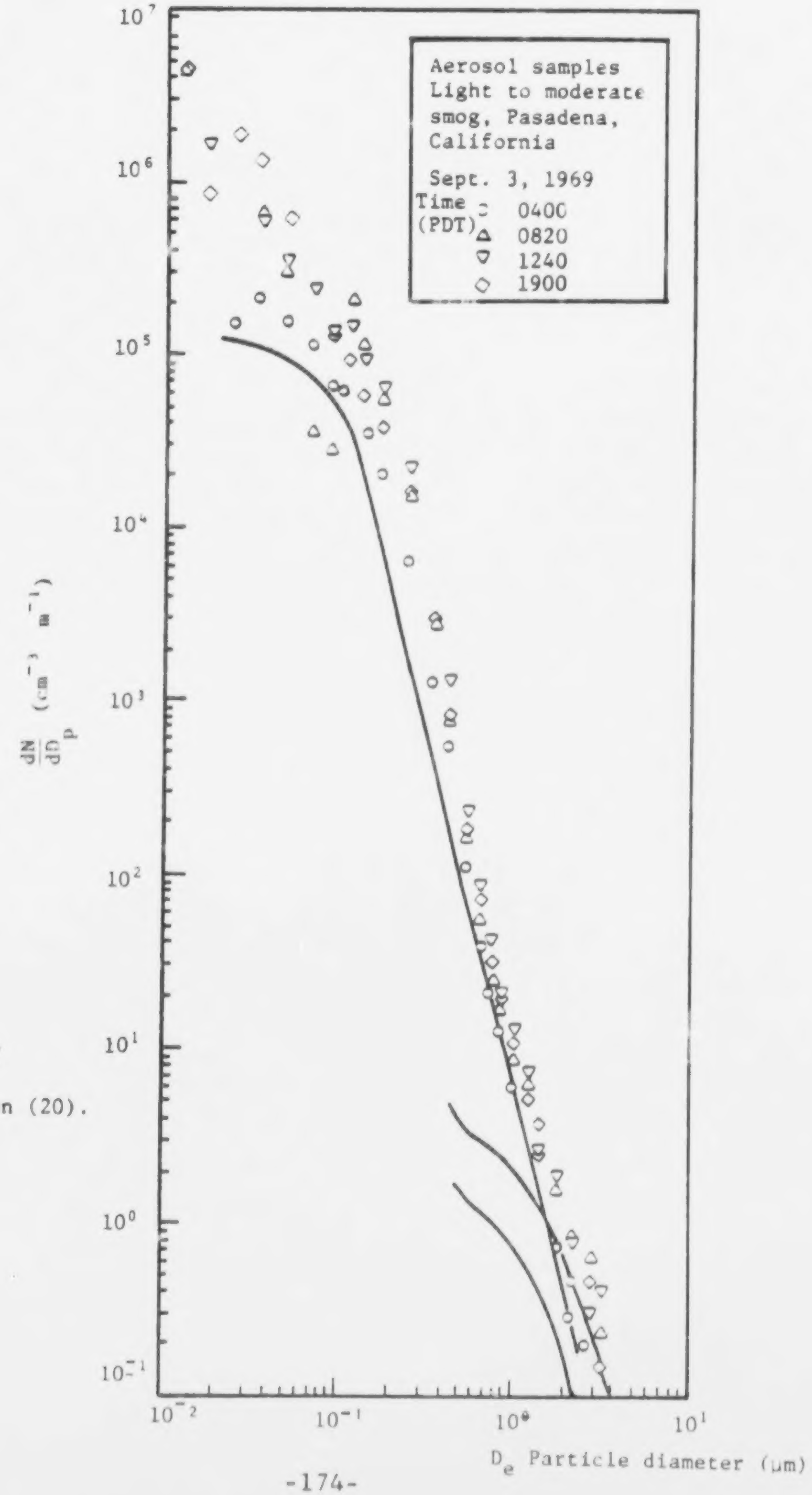

Figure 3. Comparison of Urban and Continental Aerosol Size Distribution (20).

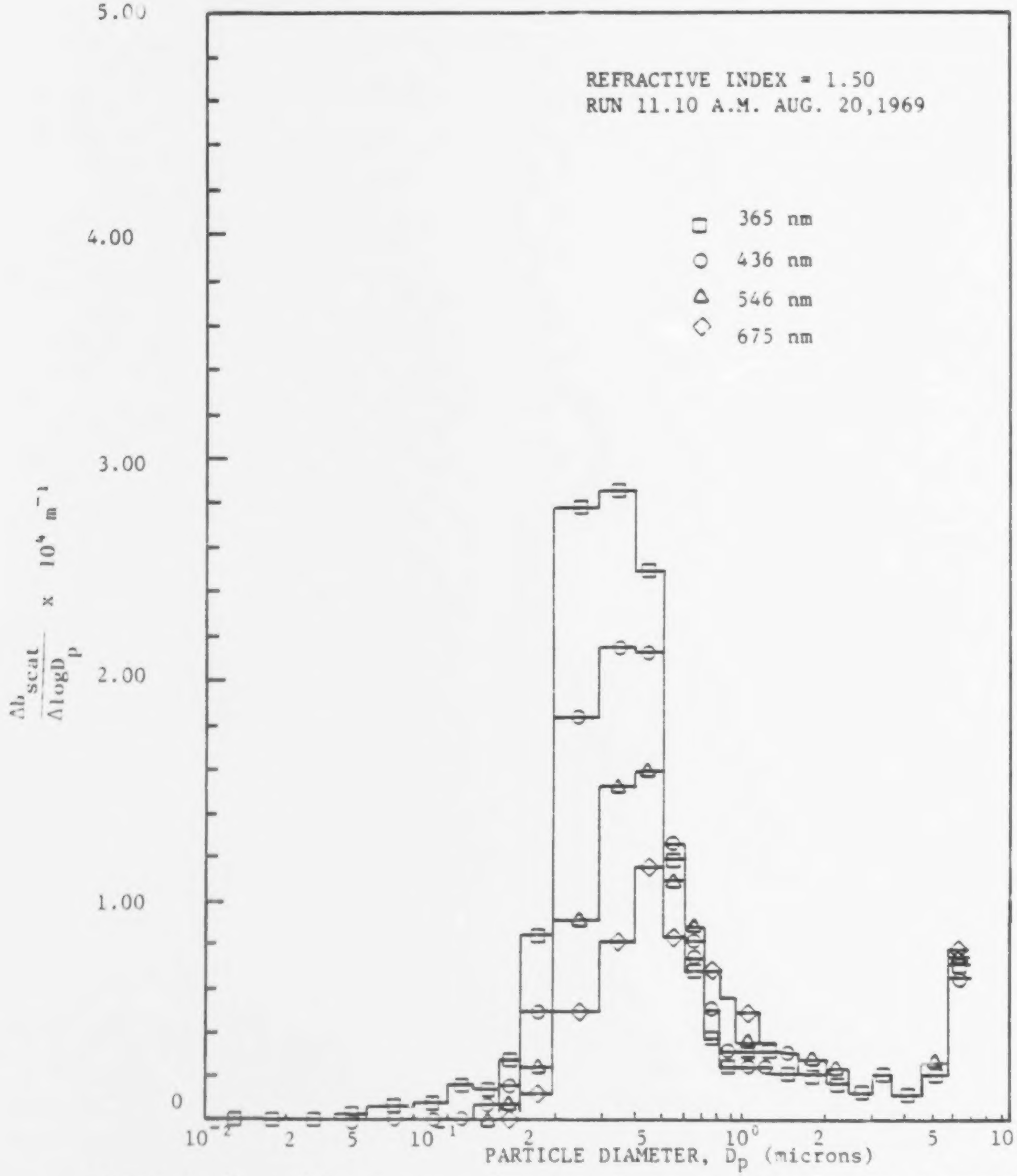

Figure 4. $\Delta b_{scat}/\Delta \log D_p$, as a function of particle diameter for a particle refractive index of 1.50.

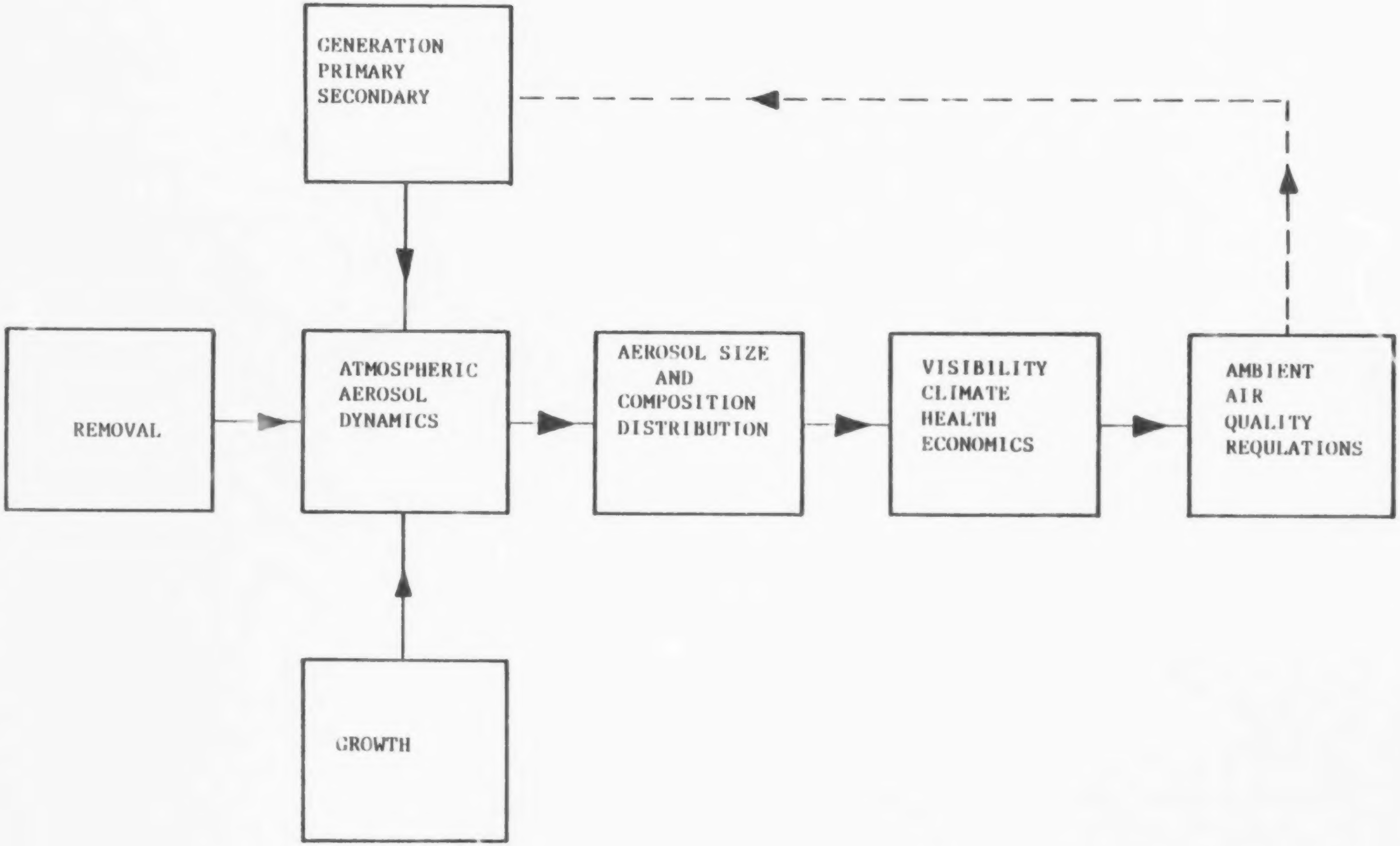
GENERATION
PRIMARY
SECONDARY
REMOVAL
ATMOSPHERIC
AEROSOL
DYNAMICS
AEROSOL SIZE
AND
COMPOSITION
DISTRIBUTION
VISIBILITY
CLIMATE
HEALTH
ECONOMICS
AMBIENT
AIR
QUALITY
REQULATIONS
GROWTH

FIGURE 5. RELATIONSHIP OF CONTROL STRATEGIES TO ATMOSPHERIC AEROSOL DYNAMICS AND CHARACTERISTICS

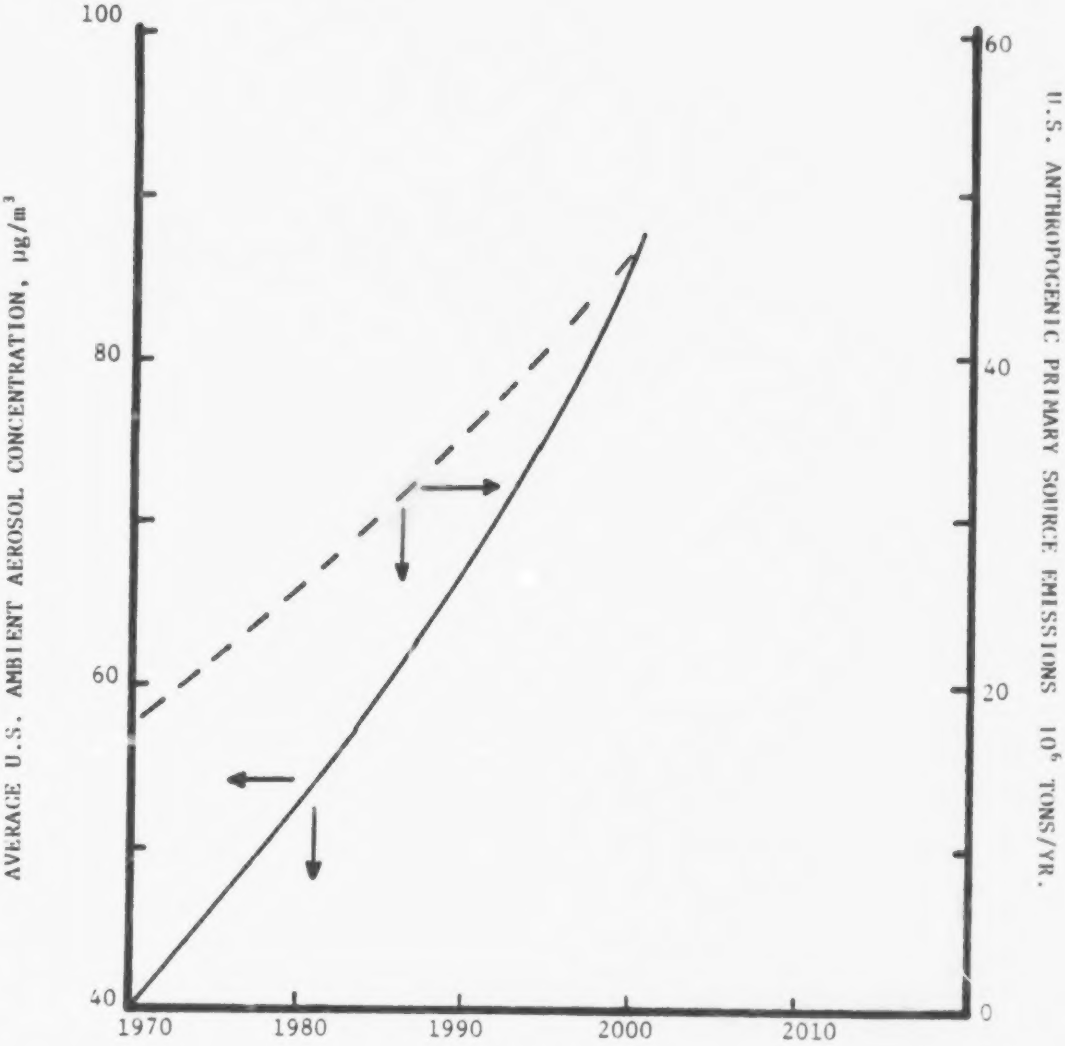

FIGURE 6. PROJECTION OF AVERAGE U.S. AMBIENT AEROSOL CONCENTRATION DUE TO ANTHROPOGENIC PRIMARY SOURCE EMISSIONS.

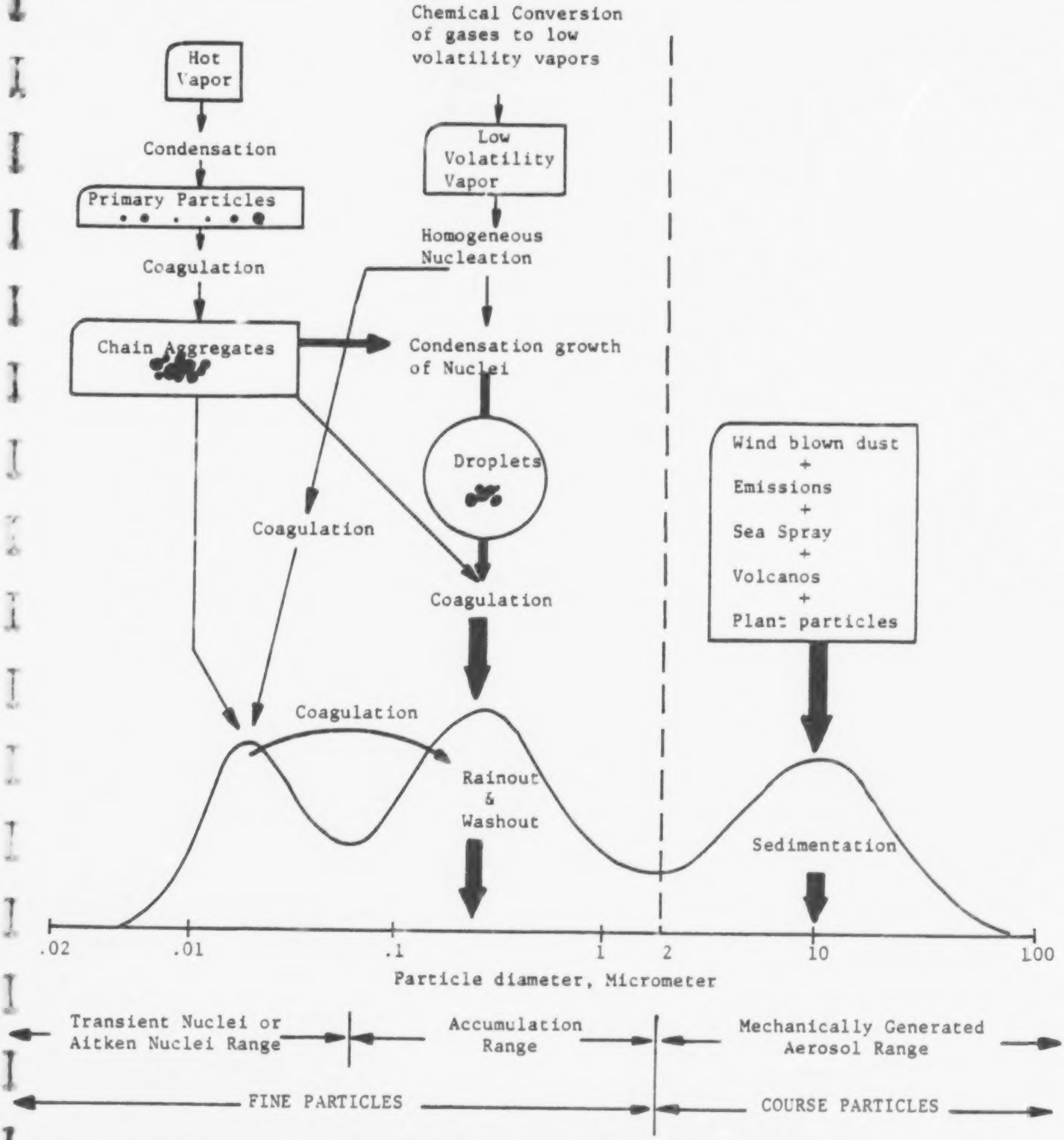
Chemical Conversion of gases to low volatility vapors
Hot Vapor
Condensation
Primary Particles
Coagulation
Low Volatility Vapor
Homogeneous Nucleation
Chain Aggregates
Condensation growth of Nuclei
Droplets
Coagulation
Coagulation
Wind blown dust + Emissions + Sea Spray + Volcanos + Plant particles
Coagulation
Rainout & Washout
Sedimentation
.02
.01
.1
1
2
10
100
Particle diameter, Micrometer
Transient Nuclei or Aitken Nuclei Range
Accumulation Range
Mechanically Generated Aerosol Range
FINE PARTICLES
COURSE PARTICLES

FIGURE 7. SCHEMATIC OF AN ATMOSPHERIC AEROSOL SURFACE AREA DISTRIBUTION SHOWING PRINCIPAL MODES, MAIN SOURCES OF MASS FOR EACH MODE, AND THE PRINCIPAL PROCESSES INVOLVED IN INSERTING MASS IN EACH MODE, AND THE PRINCIPAL REMOVAL MECHANISMS. (48).

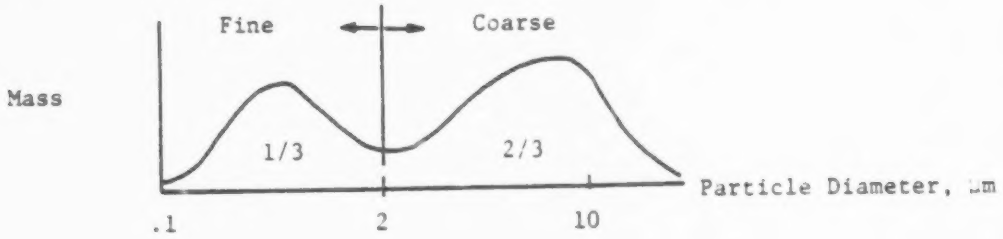

Figure 8. Atmospheric aerosol mass size distributions are usually bimodal with about one-third of the total mass in the fine particle (or submicron) mode and two-thirds in the coarse particle mode. (48)

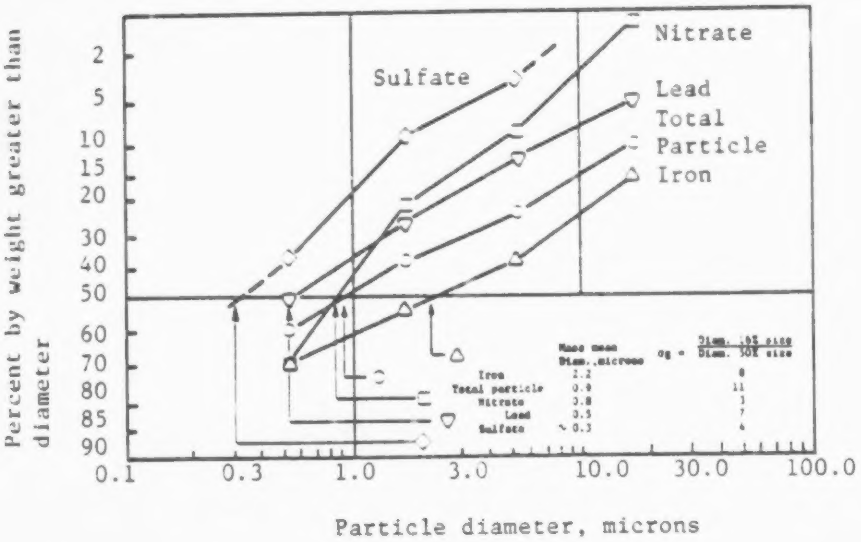

Figure 9. Average Size Distribution for 10 Impactor Samples. (63)

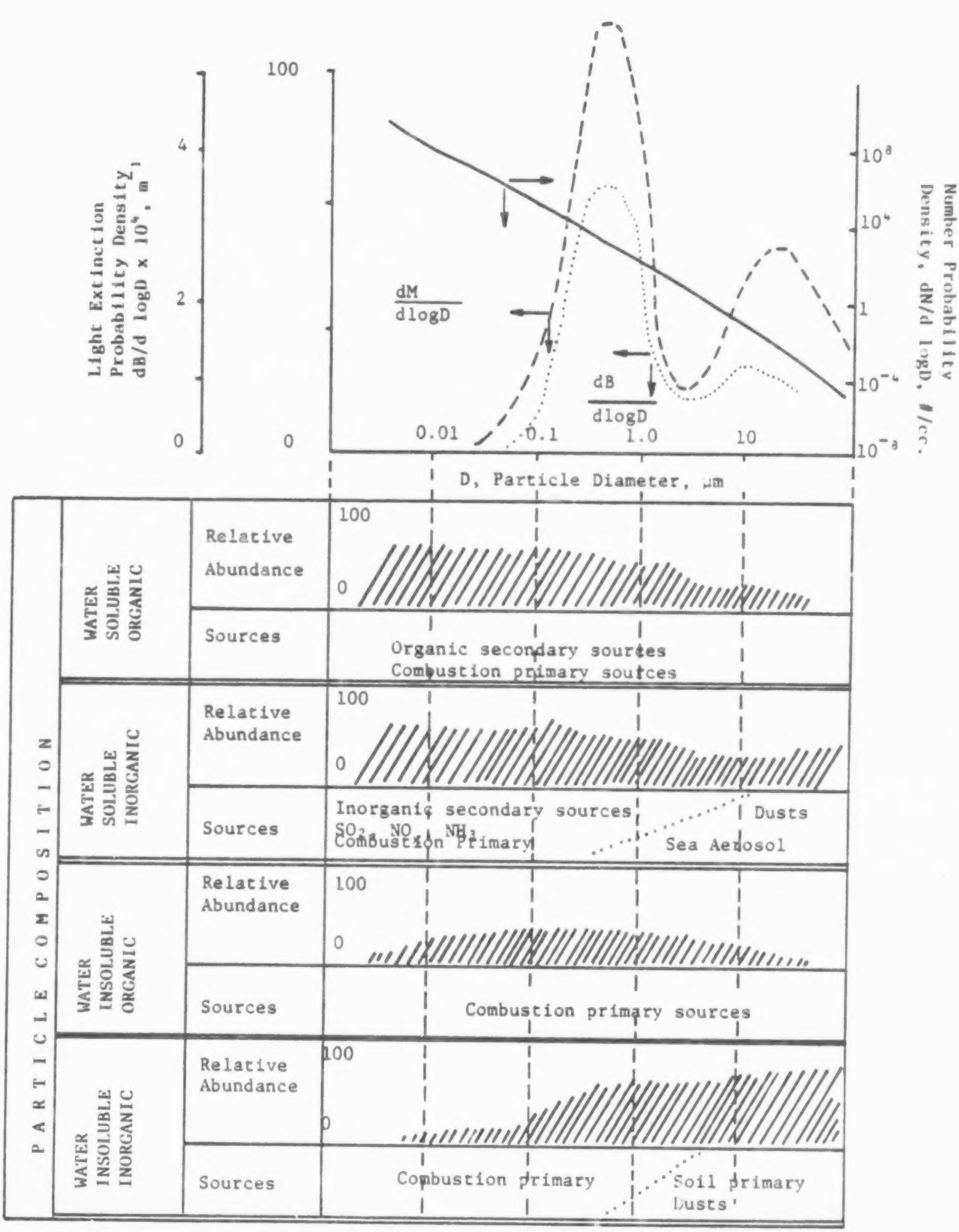

Figure 10. EXAMPLE OF PARTICLE SIZE AND COMPOSITION DISTRIBUTIONS IN PHOTOCHEMICALLY ACTIVE URBAN AIR.

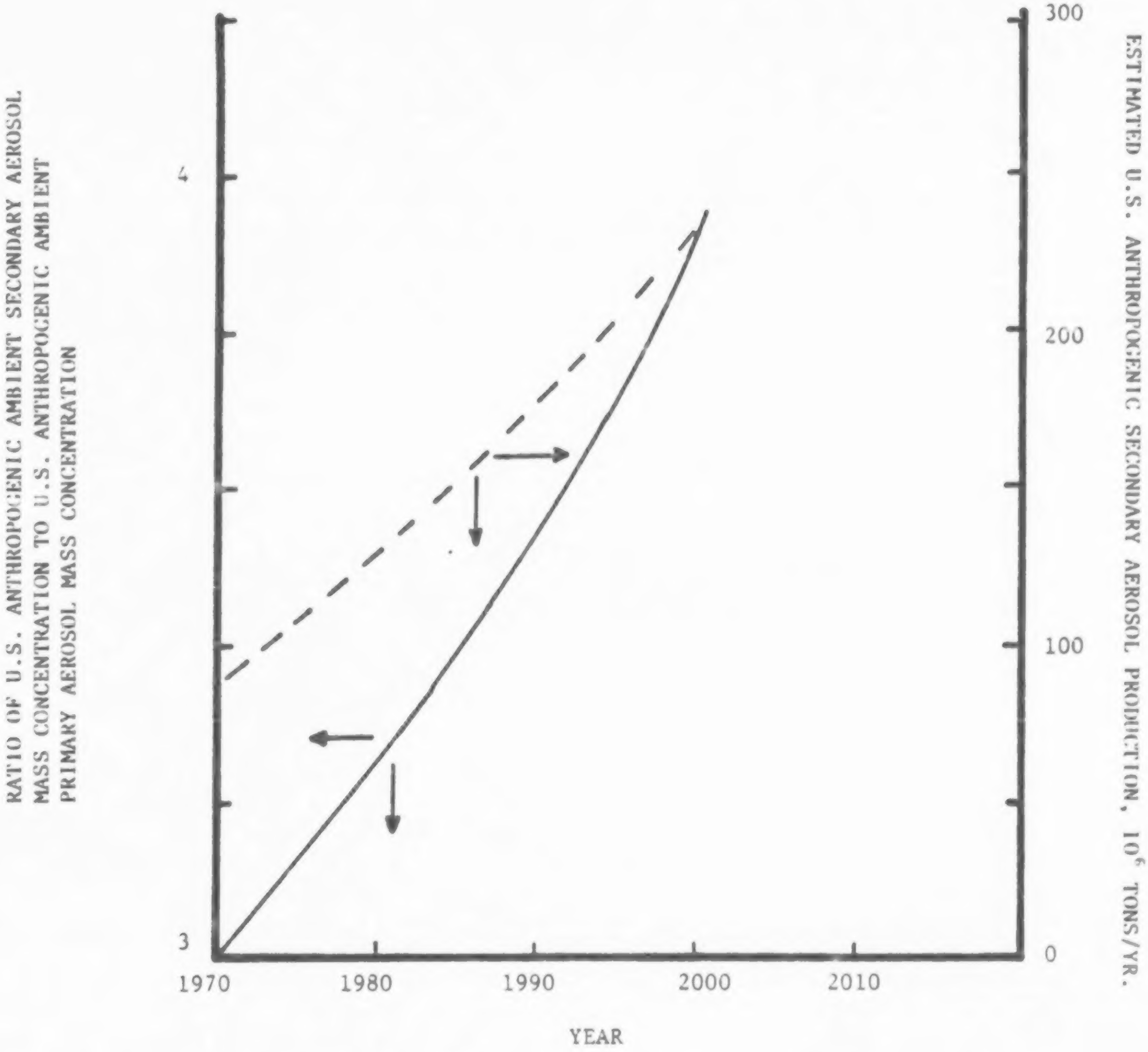

Figure 11. PROJECTION OF AVERAGE U.S. AMBIENT AEROSOL MASS CONCENTRATION DUE TO ANTHROPOGENIC SECONDARY SOURCE EMISSIONS.

TABLES

Table 1. OBSERVED RELATIONS BETWEEN POLLUTANT LEVELS AND HEALTH EFFECTS

Pollutant	Concentration level producing adverse health effects	Adverse health effects	Reference
Particulate matter and sulfur oxides	50-100 $\mu g/m^3$ particulates (annual geometric mean)	Increased death rates for persons over 50 years of age.	Winkelstein (5)
	130 $\mu g/m^3$(0.046 ppm) of SO_2 (annual mean) accompanied by particulate concentrations of 130 $\mu g/m^3$	Increased frequency and severity of respiratory diseases in schoolchildren	Douglas and Wallter (6)
	190 $\mu g/m^3$ (0.068 ppm) of SO_2 (annual mean) accompanied by particulate concentrations of about 177 $\mu g/m^3$	Increased frequency and severity of respiratory diseases in schoolchildren	Lunn, et al. (7)
	105-265 $\mu g/m^3$(0.037-0.092 ppm) of SO_2 (annual mean) accompanied by particulate concentrations of 185 $\mu g/m^3$	Increased frequency of respiratory symptoms and lung disease	Petrilli, et al. (8)
	140-260 $\mu g/m^3$ (0.05-0.09 ppm) of SO_2 (24-hr. average).	Increased illness rate of older persons with severe bronchitis	Carnow, et al. (9)
	300-500 $\mu g/m^3$ (0.11-0.19 ppm) of SO_2 (24-hr mean) with low particulate levels	Increased hospital admissions for respiratory disease and absenteeism from work of older persons	Brasser, et al. (10)
	300 $\mu g/m^3$ particulates for 24 hr. accompanied by SO_2 concentrations of 630 $\mu g/m^3$ (0.22 ppm)	Chronic bronchitis patients suffering acute worsening of symptoms	Lawther (11)

Table 2. RELATION BETWEEN MORTALITY OR MORBIDITY AND AIR POLLUTION INDICES AS DETERMINED BY LAVE AND SESKIN (12).

Disease	Air pollution Index	Relation
Bronchitis	Sulfur concentration; total concentration of solids	Strong relation between bronchitis mortality and several indices of air pollution. Bronchitis mortality could be reduced from 25 to 50 percent, depending on the location and pollution index, by reducing pollution to the lowest level currently prevailing in the region.
Lung cancer	Urban versus rural areas	With adjustments made for age and smoking history, incidence of lung cancer is about 1.5 times as great in urban as in rural areas.
Nonrespiratory tract cancer	Suspended particles; smoke density	Stomach cancer significantly related to a particulate deposit index.
Cardiovascular disease	Urban versus rural areas	A substantial abatement of air pollution would lead to 10 to 15 percent reduction in the mortality and morbidity rates for heart disease.
Total respiratory disease	Sulfates; particles	Strong relation between incidences of emphysema and bronchitis and air pollution. Also relations for pneumonia and influenza cited.
Total mortality rate	Sulfates; particles	A 10 percent decrease in the minimum concentration of particles would decrease the total death rate by 0.5 percent. A 10 percent decrease in the minimum concentration of sulfates would decrease the total death rate by 0.5 percent.

Table 3. BEST JUDGEMENT ESTIMATES OF POLLUTANT THRESHOLDS FOR ADVERSE EFFECTS OF LONG-TERM EXPOSURES (13)

	Threhold (annual average), $\mu g/m^3$		
Effect	Sulfur dioxide (80)[a]	Total suspended particulates (75)[a]	Suspended sulfates (no standard)[a]
Increased prevalence of bronchitis in adults	95	100	15
Increased acute lower respiratory disease in children	95	102	15
Increased frequency of acute respiratory disease in families	106	151	15
Decreased lung function of children	200	100	13

[a] National Primary Air Quality Standard. The particulate standard is a geometric mean; the equivalent arithmetic mean would be about 85 $\mu g/m^3$.

Table 4 BEST JUDGMENT ESTIMATES OF POLLUTANT THRESHOLDS FOR ADVERSE EFFECTS OF SHORT-TERM EXPOSURES (13)

	Threshold, $\mu g/m^3$		
Effect	Sulfur dioxide (365)[a]	Total suspended particulate (260)[a]	Suspended sulfates (no standard)[a]
Aggravation of cardiopulmonary symptoms in elderly	> 365	80-100	8-10
Aggravation of asthma	180-250	70	8-10

[a] National Primary Air Quality Standard.

Table 5. POSSIBLE EFFECTS PRODUCED BY INHALED PARTICULATE MATTER AFTER DEPOSITION IN RESPIRATORY TRACT COMPARTMENTS (16)

Compartment in which Deposition Occurs	"Soluble" Particle	"Insoluble" Particle	
Nasopharyngeal	1. Damage mucosa and cilia 2. Alergic response	1. Transferred to G.I. tract 2. Removed with sputum 3. Alergic response	
Tracheobronchial	1. Reflex bronchoconstriction 2. Alergic response 3. Damage to mucosa and cilia	1. Short-term clearance to G.I. tract. 2. Removed with sputum	
Pulmonary	1. Damage alveolar epithelium 2. Peripheral respiratory unit constriction	Long-term Retention	
		Peripheral airway and alveolar constriction	1. React with tissue to cause local effects 2. Remain in tissue (inert) Transported to lymph nodes
		Short-term Retention	
		Peripheral airway and alveolar constriction	Phagocytized and transpo-ed to terminal bronchioles with subsequent clearance from T-B Compartment.

Table 6: Speculated Global Inventory of Major Sources after Adjustment to Known Compostion of Aerosols (65)

	Total Production Rate (tons day^{-1})	(% by Wt.)
1. Primary		
Dust Rise by Wind	10^6	21.
Sea Spray (Sea SO_4^{2-})	2×10^6	42. (3.)
Extraterrestrial	550	0.01
Volcanic Dust	10^4	0.2
Forest Fires	4×10^5	8.8
Combustion & Industrial	3×10^5	6.
2. Secondary		
Vegetation	2×10^5	4.
Anthropogenic Hydrocarbons	10^4	0.2
Sulfur Cycle	6×10^5	13.
Nitrogen Cycle		
Ammonia	10^5	2.
$NO_x \rightarrow NO_3^-$	2×10^5	4.
Volcano (Volatiles)	10^3	.02
ADJUSTED TOTAL	4.7×10^6	100.
ANTHROPOGENIC	4.3×10^5	9.

Table 7

Projections of particulate emission levels (emissions in 10⁶ tons/year). (26)

Industry	1970			1980			1990			2000		
	1	2	3	1	2	3	1	2	3	1	2	3
Electric utilities	3.36	3.18	2.34	4.30	3.01	1.10	5.98	2.57	0.76	[illegible]	[illegible]	[illegible]
Industrial power generation	3.22	3.00	2.69	4.12	2.67	0.69	4.12	1.55	0.65	[illegible]	[illegible]	[illegible]
Crushed stone	5.71	4.72	4.79	9.66	0.79	0.43	15.64	0.70	0.41	[illegible]	[illegible]	[illegible]
Agricultural operation	1.84	1.67	1.58	2.05	0.88	0.27	2.76	0.32	0.17	2.47	[illegible]	0.12
Iron and steel	1.31	1.24	1.19	1.33	0.31	0.81	1.40	0.38	0.25	[illegible]	[illegible]	0.13
Cement	0.96	0.87	0.80	1.39	0.65	0.24	1.90	0.32	0.19	2.13	0.23	0.20
Pulp mills	0.56	0.50	0.47	0.81	0.35	0.16	0.93	0.20	0.13	1.24	0.17	0.12
Lime	0.65	0.59	0.56	1.04	0.39	0.17	1.22	0.22	0.15	1.38	0.22	0.15
Primary nonferrous metals												
Aluminum	0.17	0.14	0.12	0.29	0.13	0.07	0.39	0.11	0.07	0.47	0.10	0.05
Copper	0.34	0.29	0.28	0.42	0.08	0.01	0.48	0.02	0.01	0.55	0.01	0.01
Zinc	0.05	0.04	0.04	0.05	0.02	0.01	0.05	0.01	0.01	0.06	0.01	0.01
Lead	0.03	0.03	0.03	0.04	0.01	0.00	0.04	0.01	0.00	0.04	0.00	0.00
Clay	0.54	0.43	0.41	0.79	0.11	0.06	1.17	0.08	0.05	1.77	0.06	0.04
Fertilizers	0.30	0.26	0.23	0.35	0.12	0.05	0.42	0.10	0.04	0.50	0.08	0.04
Phosphate rock	0.06	0.05	0.05	0.07	0.01	0.01	0.08	0.01	0.01	0.09	0.01	0.01
Asphalt	0.22	0.20	0.17	0.32	0.16	0.08	0.48	0.15	0.10	0.73	0.17	0.14
Ferroalloys	0.16	0.15	0.14	0.19	0.09	0.02	0.22	0.03	0.02	0.25	0.03	0.01
Iron foundries	0.15	0.14	0.13	0.18	0.08	0.03	0.19	0.03	0.02	0.21	0.03	0.02
Secondary nonferrous metals												
Copper	0.06	0.06	0.05	0.07	0.02	0.00	0.09	0.00	0.00	0.09	0.00	0.00
Aluminum	0.07	0.06	0.06	0.08	0.02	0.00	0.11	0.01	0.00	0.12	0.00	0.00
Lead	0.00	0.00	0.00	0.01	0.00	0.00	0.01	0.00	0.00	0.01	0.00	0.00
Zinc	0.01	0.01	0.00	0.01	0.00	0.00	0.01	0.00	0.00	0.01	0.00	0.00
Coal cleaning	0.11	0.10	0.09	0.16	0.09	0.08	0.22	0.10	0.09	0.23	0.12	0.11
Carbon black	0.09	*	*	0.05	*	*	0.01	*	*	0.01	*	*
Petroleum	0.05	0.04	0.04	0.07	0.03	0.02	0.11	0.02	0.01	0.13	0.02	0.02
Acids	0.02	0.02	0.01	0.03	0.01	0.00	0.05	0.01	0.00	0.07	0.01	0.00

* Not calculated because Channel Process is being phased out.

Table 8 COMPOSITIONS OF EMISSIONS FOR SOME CHICAGO POLLUTION SOURCES, PERCENT (39)

	Auto	Cement	Coal and coke	Fuel oil	Iron and steel	Soil
Al		2.5	14.0	5.0	2.4	5
As			0.016			
Br	7.9					
Ca		44	4.0	0.4	5.4	0.8
Cd			0.004			
Cl	6.8					
Co			0.009	0.15		0.002
Cr			0.03	0.12		0.005
Cu			0.04	0.16	1.6	0.003
Fe	0.4	2.7	7.0	2.5	38.7	3
Hg			0.00002			0.00004
K				0.10		2
La						0.004
Mg		1.2	0.8	0.3	1.6	0.7
Mn			0.024	0.03	2.4	0.03
Na			0.4	1.5		0.6
Ni			0.04	6.0		0.005
Pb	40		0.12	0.18		0.005
Sc						0.0015
Ti			0.9	0.03		0.3
V			0.08	2.5		0.007
Zn	0.14		0.09	0.05	1.8	0.01

Table 9: Primary Source Emission Contribution To Ambient Aerosol Mass

Primary Sources, 10^6 Tons/yr					Mass Median Diameter, μm		Inverse Particle Residence time
Industry	1970	1980	1990	2000	1970 Control	(Ref.)	[illegible]
Coal Fired Elect. Utility	3.36	4.40	5.98	7.65	2	(37)	115
Ind. Power	3.22	4.12	4.12	4.00	2	(36)	115
Crushed Stone	5.71	9.66	15.64	25.16	10	(36)	625
Agric. Opn.	1.84	2.05	2.26	2.47	10	(36)	625
Iron & Steel	1.31	1.38	1.40	1.48	0.4	(36)	20
Cement	0.96	1.39	1.90	2.43	3.0	(36)	175
Pulpmills	0.56	0.81	0.93	1.24	1.0	(36)	54
Lime	0.65	1.04	1.22	1.38	2.0	(36)	115
Non Ferrous Metals	0.73	0.97	1.18	1.36	1.0	(36)	54
Clay	0.54	0.79	1.17	1.77	3.0	(36)	175
Fertilizers	0.30	0.35	0.42	0.50	1.0	(36)	54
Phosphate rock	0.06	0.07	0.08	0.09	2.0	(36)	115
Asphalt	0.22	0.32	0.48	0.73	1.0	(36)	54
Ferro alloys	0.16	0.19	0.22	0.25	0.4	(36)	20
Iron Foundries	0.15	0.18	0.19	0.21	0.4	(36)	20
Coal Cleaning	0.11	0.16	0.22	0.28	2.0	(36)	115
Petroleum	0.05	0.07	0.11	0.16	0.5	(36)	27
Acids	0.02	0.03	0.05	0.07	0.4	(36)	20
Solid Waste Disposal	1.4	1.4	1.5	1.6	0.3	(57)	15
Construction Dust	0.8	1.1	1.4	1.7	5	(57)	300
Transportation-Combustion	1.2	1.6	2.0	2.4	0.4	(57)	20
Transportation-Tire Dust	0.3	0.4	0.5	0.6	3.0	(57)	175
Transportation-Road Dust	1.0	1.34	1.68	2.0	5.0	(57)	300
TOTAL	24.65	33.82	44.65	59.53			

Table 9: Continued

Industry	Total Mass of Ambient Suspended Particulate Matter, 10^6 Tons 1970	1980	1990	2000
Elect. Utility	0.029	0.038	0.052	0.066
Industrial Power	0.028	0.036	0.05	[illegible]
Crushed Stone	0.0091	0.015	0.025	[illegible]
Agricultural Operations	0.003	0.003	0.004	[illegible]
Iron & Steel	0.065	0.069	0.070	[illegible]
Cement	0.005	0.008	0.011	[illegible]
Pulp Mills	0.010	0.015	0.017	0.023
Lime	0.006	0.009	0.010	0.012
Non Ferrous Metals	0.013	0.018	0.022	0.025
Clay	0.003	0.004	0.007	0.010
Fertilizers	0.006	0.006	0.008	0.009
Phosphate Rock	-----	-----	----	0.001
Asphalt	0.004	0.006	0.009	0.013
Ferro alloys	0.008	0.009	0.011	0.012
Iron Foundries	0.007	0.009	0.009	0.010
Coal Cleaning	----	0.001	0.002	0.003
Petroleum	0.002	0.003	0.004	0.006
Acids	0.001	0.001	0.002	0.003
Solid Waste Disposal	0.093	0.093	0.100	0.106
Construction Dust	0.003	0.003	0.004	0.006
Transportation-Combustion	0.06	0.08	0.10	0.12
Transportation-Tire Dust	0.002	0.002	0.003	0.003
Transportation-Road Dust	0.003	0.004	0.006	0.007
TOTAL	0.36	0.432	0.526	0.634

Table 10. Examples of Gas Phase Reactions of Possible Importance in Condensational Growth of Atmospheric Aerosols.

Reaction	Reference
$SO_2 + \frac{1}{2}O_2 \xrightarrow{\text{Free radicals}} SO_3$	(50)
$SO_3 + H_2O \rightarrow H_2SO_4$	

$2NO_2 + H_2O \rightarrow HNO_3 + HNO_2$	(51)
$HNO_3 + nH_2O \rightarrow HNO_3 \cdot nH_2O$	

$RHR' + O_3 \rightarrow$ involatile oxygenated products	(52)

Table 11. Possible SO_2 Oxidation Reactions in Aqueous Solution Atmospheric Aerosols,(53)

Postulated Reactions (In Aqueous Phase)

$$2SO_2 + 2H_2O + O_2 \xrightarrow{\text{Cationic Catalyst}} 2H_2SO_4$$

$$2SO_2 + 2H_2O + O_2 + 4NH_3 \xrightarrow{\text{Cationic Catalyst}} 2(NH_4)SO_4$$

$$2SO_2 + 2H_2O + O_2 + 4NH_3 \rightarrow 2(NH)_4SO_4$$

$$SO_2 + O_3 + H_2O \rightarrow H_2SO_4 + O_2$$

$$2NO_2 + 2H_2O(ads) + SO_2 \rightarrow H_2SO_4 + 2HNO_2$$

$$H_2SO_3 + H_2O_2 \rightarrow H_2SO_4 + H_2O$$

$$O_3 + H_2O + SO_2 \xrightarrow[\text{Water Soluble Organic Acid}]{\text{Cationic Catalyst}} H_2SO_4 + O_2$$

ADDENDUM TO SUSPENDED PARTICULATE MATTER REVIEW MADE AT REQUEST OF ENVIRONMENTAL PROTECTION AGENCY

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August 5, 1975

PROJECTION OF AMBIENT ATMOSPHERIC PRIMARY AEROSOL MASS CONCENTRATION WITH 100% CONTROL BY 1980

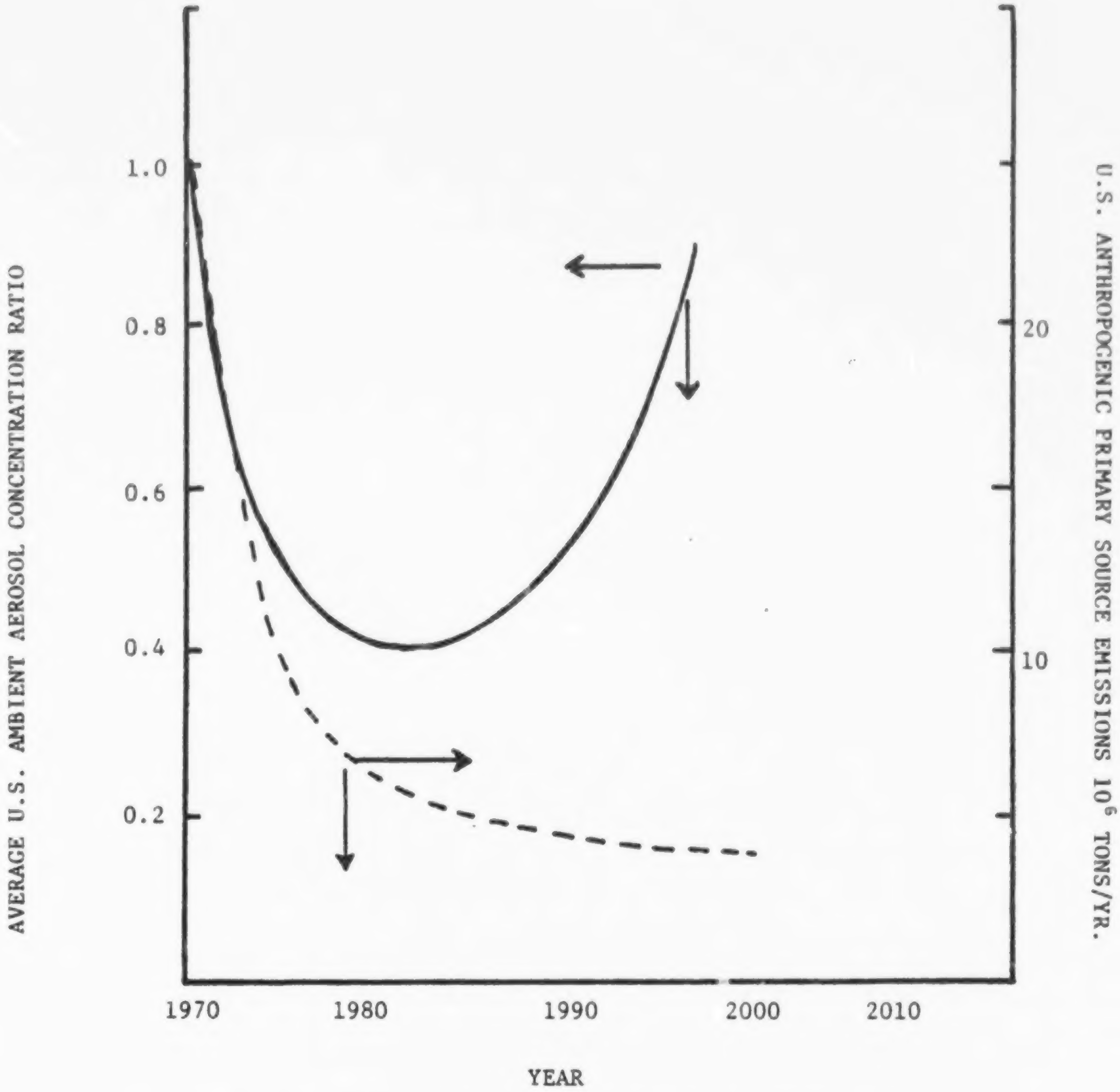
This projection of ambient atmospheric primary aerosol mass concentration assumes the control strategy proposed by Andergrift et al. In this method application of control is increased to 100% by 1980. Replacement period for existing plants is taken as ½ the IRS lifetime. Efficiency of new controls is increased based on a technological forecast curve for each industry. This equipment will be installed each year only on replaced capacity (replaced following ½ normal IRS lifetime), new capacity, and on some presently uncontrolled capacity so that the amount of control corresponds to 100% control by 1980.

With the assumption that the average efficiency of control will increase according to a technological forecast curve, it becomes a problem to forecast the corresponding change in the mass median diameters of the aerosol from the various categories of primary emissions. From the inadequate data which do exist, it appears that application of control to primary sources results in substantial decrease in the mass median diameter of a controlled emission. For example, application of current control of electric utility power plants by electrostatic precipitators results in reduction of mass edian diameter in emissions by a factor of 10. Control of cement kilns by electrostatic precipitators result in reduction of the mass median diameter by a factor of 5. Control of limestone kilns by wet scrubbers results in reduction of mass median diameter by a factor of 10. Increases in efficiency of control devices would, of course, presumably further lower the mass median diameters in these cases.

It will be assumed that by the year 2000 sources of condensation aerosols will be controlled down to a mass median diameter of 0.2 um corresponding approximately to the minima in the basic particle collection mechanisms of diffusion and impaction and of electrical mobility. Comminution sources will be assumed to have their mass median diameter reduced by a factor of 5, as a conservative estimate. The change in mass median diameter for each source category is assumed to occur linearly between 1970 and 2000, reflecting the assumptions of this projection.

The results of this projection are presented in the attached figure. The somewhat surprising feature of this projection is that although total anthropogenic primary emissions decrease, the ambient concentration due to anthropogenic primary emissions first decreases and then increases so that by the year 2000 this concentration is approximately 85% of the value in 1970. The explanation, of course, is that increased application and efficiency of control lowers the average mass median diameter of the various primary sources, thereby increasing the residence time of the particles in the atmosphere (particle residence time is believed to be a very sensitive function of the mass median diameter). At the same time, economic growth implies increases in numbers of sources to that after 1980 there is very little decrease in the mass emission rates of the primary sources, although control efficiency is increasing.

Clearly this attempt to predict the future course of ambient atmospheric particulate levels is fraught with difficulty. However, this projection together with the initial projection of the review (based on the assumption that (efficiency of control) x (application of control) is constant, will serve to set some bounds on possible future trends of ambient atmospheric aerosols.



PROJECTION OF AVERAGE U.S. AMBIENT AEROSOL CONCENTRATION RATIO DUE TO ANTHROPOGENIC PRIMARY SOURCE EMISSIONS UNDER ASSUMPTION THAT APPLICATION BASE YEAR OF PROJECTION IS 1970.

PARTICULATE MATTER: RELATIONSHIPS BETWEEN EMISSIONS AND AMBIENT AIR QUALITY

Prepared for:

Radian Corporation
Austin, Texas

and

Control Systems Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina

by:

Lyndon R. Babcock, Jr.
Professor
University of Illinois
P.O. Box 6998
Chicago, Illinois 60680

August 1975

EXHIBITS

1. Air Quality System
2. Idealized Particle-Size Distributions
3. Primary Emission Distribution
4. Preliminary Characterizations
    a. California Composite (Before Distribution of Secondary Species)
    b. Aggregated California Composite and Nationwide Inventory
5. Detailed Characterizations
    a. California Composite
    b. Nationwide (Unnormalized)
    c. Nationwide (Normalized)
6. California-Composite Characterization Diagram
7. Nationwide Characterization Diagram
8. Summary Comparison

SUMMARY

This report addresses source-characterization relationships of atmospheric aerosols; fine particulate matter and secondary pollutants receive emphasis. The report is directed to individuals involved in defining aerosol-related research priorities and control strategies.

Existing published information has been used to generate the central results, which consist of two detailed source-species-size characterizations, one for a composite of five California cities and a second, more representative of nationwide emissions. A summary of the characterizations follows on Page 199.

Significant differences between the two characterizations can be noted, but in each case, combustion-and-industry and natural-and-miscellaneous have been identified as the largest source categories. Secondary pollutants comprise a significant fraction of both totals, and primary fine particulate matter from stationary sources comprises a sizeable constituent in the nationwide characterization (16 percent of the total).

In each characterization, the total aerosol mass has been specified with regard to source, species, and particle size. This "closure" was accomplished only after incorporating many assumptions into the calculations. The methodology and assumptions are clearly defined, and readers are encouraged to critically review the work and to suggest alternative approaches and conclusions.

The literature review was performed in an unusual manner, in that experts in the fields of atmospheric chemistry and aerosol characterization reviewed a common body of pertinent literature from which three separate reports were individually prepared. These reports served as inputs from which the writer arrived at the discussion and conclusions presented herein.

SUMMARY COMPARISON

Category	California	Nationwide
Combustion and Industry	26	49
Transportation	23	15
Natural and Miscellaneous	39	24
Water	12	12
TOTAL:	100	100
Secondary PM	32	25
Primary fine PM (from stationary sources)	4	16
Other Primary fine PM	8	5
Large PM	44	42
Water	12	12
TOTAL:	100	100

INTRODUCTION

The Control Systems Laboratory (CSL) of the U.S. Environmental Protection Agency (EPA) has a responsibility for the development of technology for the control of air pollutant emissions from stationary sources. Major research programs sponsored by CSL are directed toward improved control of sulfur dioxide, nitrogen oxides, hydrocarbons, and particulate matter (PM), as well as toward control problems associated with chemical, metallurgical, and energy processes.

Technology for the control of large-size PM (above two micron in diameter) has been available for many years; therefore, in addition to conventional particulate control, a CSL program emphasizes novel approaches for control of fine PM. The smaller-sized particles are much more difficult to control, remain suspended in the ambient atmosphere for longer periods of time, are largely responsible for visibility degradation, and are thought to be largely responsible for the adverse health effects associated with PM.

Further, small particles have a high surface area per unit mass, and this surface may catalyze gas-to-particulate reactions. Also, several individual toxic trace metal species such as lead, zinc, vanadium, etc., appear to be concentrated in the smaller particles. Another cause for concern may be related to small particles of combustion carbon which have been found to remain for long periods at high altitudes in the troposphere. It has been postulated that these particles absorb solar radiation with the resulting layer of warmer air causing a semipermanent increase in atmospheric stability.

Clearly, there are health, esthetic, and possibly even climatic, incentives to reduce ambient levesl of fine PM at many locations throughout the nation, and the CSL fine PM program is directed toward that goal. However evidence is now accumulating which indicates that significant amounts of fine PM can be formed in the atmosphere. In some locations, this secondary PM, formed from gaseous precursors, may be the dominant PM species. Few deny the presence and significance of secondary PM constituents, but we seem to be quite a ways away from having usable quantitative source-ambient relationships, even for relatively heavily studied areas such as California.

In the midst of this uncertainty, CSL seeks to allocate its resources in an optimal manner. Some have suggested that, in light of the secondary-PM evidence, the CSL fine particulate program should be deemphasized. However, certain questions should be answered before decisions on CSL priorities can be meaningfully made: What are the quantitative size and species characterizations of PM? What are the original sources of this PM? How much is primary; how much is secondary? How much is derived from stationary sources versus mobile and the so-called "natural" sources? How do the findings vary from location to location?

This report summarizes an unusual short-term study which has attempted to address these questions. Elsewhere, an exciting long-range diverse research program funded by the Atmospheric Aerosol Research Section (AARS) of the Chemistry and Physics Laboratory of EPA is continuing. In contrast, the short-term study described herein is confined to examination, interpretation, and integration of existing results. Our short-term study may serve to suggest additional experimental research to AARS.

Method

A common body of pertinent literature was identified by personnel of CSL, AARS, and Radian Corporation. (These references are listed on pages 241-246. Experts in the fields of aerosol characterization and atmospheric chemistry agreed to independently review this literature, and to independently prepare three reports, incorporating their own knowledge and experiences into interpretations of the literature information. The consultants included: (1) G.M. Hidy and P.K. Mueller, Environmental Research and Technology, Inc., Westlake Village, California; (2) J.P. Lodge, Consultant in Atmospheric Chemistry, Boulder, Colorado; (3) J.R. Brock, University of Texas, Austin, Texas.

More recently, at the request of CSL personnel, a fourth central input item, a paper by Gartrell and Friedlander was added to this study.

I agreed to study the common body of literature and the four input reports (citations listed on page 37) and to summarize and interpret the findings for use by CSL personnel. Such is the purpose of this summary report. It is suggested that it be read with close referral to the four input reports. Duplication of material included in the input reports has been kept to a minimum in this summary report.

Source-to Ambient System

Before discussing specific findings, it seems desirable to define some terminology and relationships.

Some basic aspects of the air quality system can be related as shown on Exhibit 1. Flows of pollutants are indicated by solid lines, while other influences are indicated by dashed lines. Our concern is with the air quality experienced by receptors. The presence of meteorological variables, transformations, and decay and deposition mechanisms multiplies the difficulties in relating emissions to ambient air quality. Transformations of many types are feasible; this report is largely concerned with the transformation of gaseous pollutants, such as sulfur dioxide and hydrocarbons, into solid and liquid fine PM, such as acid sulfates and oxidized organic matter.

On Exhibit 1, the two areas of greatest uncertainty are indicated by the ellipses. Toward the left, four paths are indicated for emissions: emissions may reach human receptors directly; emissions may decay or otherwise remove themselves from the atmosphere without reaching human receptors; emissions may undergo various kinds of transformations; or certain species of emissions may provide catalysts which promote the extent of transformations. Similarly, on the right-hand side of Exhibit 1, transformed pollutants may either influence the air quality experienced by receptors, or can bypass and go directly to a decay or deposition sink. Note that transformations are influenced not only by airborne catalysts, but by solar radiation and meteorology. In fact, meteorology influences almost every aspect of the source-to-sink process. Also note again that there are two feasible paths by which pollutants can circumvent human receptors. Quite clearly, all emissions need not affect all receptors.

The paths to decay can be seen to be significant aspects of the air quality management system. Yet many control policies seem to ignore these aspects, while other control policies generate interesting questions. For example, tall stacks are employed to reduce adverse effects of pollutants such as sulfur dioxide upon nearby receptors. Yet tall stacks reduce the likelihood of direct sulfur dioxide deposition (a relatively rapid process compared to sulfate deposition). By increasing atmospheric residence time, the tall stack provides the opportunity for airborne transformation as well as for eventual decay. A major concern then is extent to which toxic decay intermediates, such as acid sulfates, affect receptors prior to eventual ultimate decay and deposition.

Most workers in air-quality-management-related fields are attempting to define some aspect of Exhibit 1; our source-receptor study is no exception. The large number of workers and the remaining large number of unanswered questions are indicative of the complexity of the task. The limited effort summarized in this report is directed at integrating existing information on transformations, etc., toward development of some presently-useful source-receptor relationships.

The conventional approach has been to start with emissions, add in some meteorological modeling and arrive at estimates of effects of various sources upon receptors. This "source-to-receptor" approach is clearly inadequate if complex transformations and decay mechanisms are involved. Thus, more recently, "receptor-to-source" methodologies have begun to evolve. Comprehensive characterization of ambient particulate matter can supply evidence as to the extent of transformation and removal as well as to the original sources.

Most workers have tended to emphasize one approach or the other. There have been a few notable exceptions, and the goal of this study is to explore and extend efforts to integrate the two approaches. It is evident that neither approach alone can define the complex source-receptor system described on Exhibit 1.

Other Definitions

Several types of PM are discussed in the input reports and in this summary report. Some definitions and comments follow:

Bimodal distribution. Most aerosol scientists now agree that ambient aerosols tend to be bimodal, with the minimum occurring between one and two micron. An idealized bimodal distribution is shown on Exhibit 2. The Brownian-motion mechanism seems to be in part responsible for the minimum. That is, small particles can grown by coagulation (impacting and adhering to each other), but the Brownian motion which generates coagulation, decreases as the particles grow larger. It seems likely that the coagulation process functions for primary as well as secondary PM. Several shapes can be postulated for the primary contribution to the fine PM mode (dashed curves 1, 2 and 3 on Exhbiti 2). The term "fine PM", in contrast to "large PM', as used herein refers to PM smaller than two micron in diameter. Fine PM may be either primary or secondary.

Primary and secondary particulate matter. PM emitted directly from sources and remaining relatively unchanges chemically is termed primary. However, it is possible to postulate that these particles, if small enough, grow through coagulation, or that these small particles grow when gaseous species react on their surfaces. A major question is the size distribution of the primary fraction, particularly at the fine end of the distribution. (See Exhibit 2.). Combustion processes are major contributors to primary fine PM, and comminution processes may make a limited contribution.

Those particles formed in the atmosphere from gaseous precursors are termed secondary. Even here the definition is uncertain. Certain species may condense shortly after leaving a stack, undetected by a stack emission test, but soon existing as PM, virtually at the point of emission. It is generally agreed that secondary particles are generated in very small, almost molecular sizes, and they grow via coagulation until the Brownian motion mechanism ceases. However, it is also possible to postulate gaseous precursors adding to existing fine or even to large PM. Thus, an unknown amount of the large-size fraction could be of secondary origin.

Combustion, comminution, and natural sources. Combustion processes produce small particles, less than one micron in size (Fennelly, 1975). A major species is the relatively inert combustion carbon. These particles are not included in a benzene-soluble or other "organic" characterization. Similarly, fine PM other than carbon can be formed during high temperature condensation or combustion. Many varieties of trace metals are likely. Vanadium is of particular interest because of its presence in fuel oil and its possible activity as a catalyst which promotes the oxidation of sulfur dioxide.

Comminution processes (such as crushing and grinding) tend to produce large particles. Unlike coagulation, during comminution, probabilities are higher that large particles will impact on each other. It is often assumed that comminution processes produce no fine PM; yet there seems no theoretical reason for an abrupt truncation in a comminution distribution. Rather, one would expect an asymptotic decay as particle size decreases. Lack of definition may result from inadequate fine-size characterization techniques used to monitor comminution processes.

Natural or "quasi-natural" (as used by Brock) represents a third major source of particulate matter. Many "natural" sources are actually anthropogenic (manmade): for example, dust which would not be present except for intensive agriculture or other manmade alteration of the environment. The natural category as defined herein also includes reentrained or fugitive dust, that PM which becomes re-airborne after initial deposition. Such sources can sometimes be the major source in a region, and such sources can be difficult to control. It is essential that the natural contribution to ambient levels be accurately defined. Otherwise, control of anthropogenic sources may result in disappointingly-small improvements in overall ambient air quality.

Review of Input Reports

The results and discussion presented in this report are based largely upon four input reports (citations listed on page 37), three of which were prepared specifically for this study. Each report is summarized briefly below. Each report describes PM characterization and control in an individualistic, interesting way, and each should be studied carefully in its entirety to gain each author's overall message. Only those aspects closely pertaining to the source-species-size characterizations are emphasized in this summary report.

Hidy and Mueller. This report emphasizes California-based photochemical studies. Several useful experimental ambient particle size distributions are presented along with composition distributions. In these distributions unknown components varied from 17 to 70 percent of the total masses.

The chemical tracer method of Friedlander and others is proposed as the best available technique for relating ambient pollution levels back to sources. Results of the Gartrell and Friedlander paper (1975) are discussed and mixed source-species diagrams for Pasadena and Pomona are presented. Like Gartrell and Friedlander, Hidy and Mueller did not attempt to allocate the secondary species (organic, SO_4, etc.) back to sources.

Hidy and Mueller conclude by discussing the need for gas emission control in order to reduce ambient levels of secondary PM. A second report, by Hidy and Burton, "Atmospheric Aerosol Formation by Chemical Reactions" (1974) is appended to the input report. This latter report examines possible mechanisms for secondary pollutant formation.

Lodge. After an interesting historical-philosophical introduction, Lodge qualitatively discussed the sources of large particles, emphasizing the likely presence at some locations of significant or even dominant amounts of soil dust and pulverized vegetation. He made the important differentiation between "contemporaneous" carbon (that derived from recent biota) and carbon derived from fossil fuels. He concluded that "an important portion of the organic matter (in ambient PM) consisted of spores, microorganisms, pollens and comminuted plant material". Unfortunately, no size distribution data were taken in the described study.

A discussion of fine and secondary PM is also presented. This point is made that species such as sulfates need not be exclusively secondary (e.g., sulfates are contained in soil and also are emitted from fertilizer and other industrial operations).

Based upon results for Los Angeles and Milan, Lodge concluded that the secondary components could comprise as much as 40 percent of the total aerosol. However, he found the works of Harrison et al.* and Lodge (1960) to support the contention that the fraction of secondary PM could be much smaller, even in Los Angeles where Friedlander's methodology wouldn't distinguish between photochemical organic secondary aerosol and primary organic aerosol comprised largely of contemporaneous carbon.

Lodge went on to describe a Denver characterization in which "nearly 90 percent of the particles" were above one micron in size. Lodge concluded by discussing current and future standards and the need for different control strategies in different areas.

The most significant aspect of Lodge's paper applicable to this report was his insistence on consideration of the so-called natural sources and fugitive dust, and that such sources might even include significant quantities of organic matter. He concluded that such sources could dominate in areas of low humidity. Also well conveyed, was the principle that the source-species-size characterization should be expected to vary extremely in different regions of the nation, that no single characterization could be expected to be applicable across the nation.

Brock. This report provides a comprehensive review of both primary and secondary PM, including both theoretical and empirical information. Brock supports conclusions of Lodge, as well as of Hidy and Mueller, but Brock goes beyond the other consultants in addressing primary PM emissions. Estimates for 1970, 1980, 1990, and 2000 of the mass emission, particle size, and residence time in the atmosphere are given for 23 source categories. Brock uses these data to show how particle size affects the relative contribution to aerosol mass. That is, that large sources of large particles, such as "crushed stone", contribute very little effect on ambient aerosol mass.

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* Note that the other input consultants felt that the microscopy techniques employed by Harrison, Draftz, and other investigators did not adequately characterize the fine PM portion of the aerosol mass.

Gartrell and Friedlander. This paper was included belatedly in the study at the request of CSL personnel. It was not included in the original package of reports to be reviewed by the input consultants. However, Hidy and Mueller and Brock discussed the paper in their reports, and Lodge discussed an earlier related paper by Friedlander.

The paper is the most-recent published report by Friedlander and co-workers of their efforts to characterize ambient aerosols and to relate them back to sources. This paper comes closer than some of its predecessors toward obtaining closure (ie, specifying 100 percent of the aerosol mass).

The methodology involves use of chemical elements as tracers. For example, if there is lead in the aerosol, most of that lead must have originated in car exhaust. Further, proportional amounts of other species in car exhaust which also appear in the aerosol must likewise have originated as automobile emissions. In this manner, the total aerosol mass can be distributed among sources. One also can deduce that large anomalous concentrations of species such as sulfates must have been created in the atmosphere from gaseous precursors.

Gartrell and Friedlander applied their method to several California cities and these results form a basic part of the results contained in this summary report.

The methodology, still in its formative stages, has several shortcomings. First, there is no distribution between fine and large PM. Thus, one can't address Lodge's point of allocation of sulfate between primary and secondary categories. Second, Gartrell and Friedlander, in attempting to obtain 100 percent closure, allocate some of the species to sources, but for organics, sulfates, nitrates, and ammonium, they report only the percentage of each species. Apparently, the authors felt that insufficient evidence was available to make a meaningful distribution of these largely-secondary species. Thirdly, application of the methodology has been largely restricted to California cities, cities which depart considerably from the nationwide average with regard to heavy industry, coal combustion, and photochemistry.

Each of the input authors seems to support the results obtained to date from application of the Friedlander methodology, although Lodge questions the allocation of organics between secondary photochemical and contemporaneous carbon "natural" (vegetation, etc.) sources. As mentioned earlier, Gartrell and Friedlander did not attempt to distribute this category amongst sources, but apparently others have inferred that this organic category is largely attributable to the automobile.

Results

The results consist of supporting data tables (Exhibits 3-5) which lead to two characterization diagrams, one for a California composite (Exhibit 6), and the second for a more-representative nationwide approximation (Exhibit 7).

The characterizations are extensions of the results of Gartrell and Friedlander. In each case, 100 percent closure for source, species, and size is obtained by using data from Brock to define the primary fine fraction and by incorporating a multitude of assumptions.

Exhibits 6 and 7 each consist of three bar graphs. The upper bar describes the composition of the large-size particles, while the lower bar describes the fine fraction. These two bars are scaled such that when totaled together with the water, they represent 100 percent of the total suspended particulate matter (TSP) on a mass basis. The central bar represents the sources responsible for the TSP. Similarly, the length of the central source bar represents the total of all the sources of PM (including water, from whatever source). Note that the sum of the lengths of the two outer species-characterization bars is exactly the length of the central source distribution bar. On Exhibits 6 and 7, one inch is equivalent to ten percent of the TSP total. Also note that the species are related to sources by the connecting lines on the diagrams.

The reader may wish to refer directly to Exhibits 6 and 7 prior to reviewing the ensuing details as to how the exhibits were arrived at. Additional interpretation and criticism of the results is presented in the "Discussion" section of this report.

Definition of primary fine category. Primary-fine was one of the categories left undefined by Gartrell and Friedlander. Clearly, primary-fine PM is a constituent of most polluted ambient air, but little useful quantitative documentation is available; none of the input consultants estimated an amount. Recent emphases seem to have been largely directed toward definition of secondary rather than primary PM.

Brock did report the mass median diameters (MMD) for 23 source categories (his Table 9, derived largely from a 1971 Midwest-Research-Institute study). Hidy and Mueller supplemented this listing with measured distributions for marine, desert, and freeway environments. I have combined these data to arrive at size estimates for the various source categories of interest.

The fine fraction (amount below two micron) may be obtained directly by comparing areas on the graphs of Hidy and Mueller (their Figure 1). Thus:

Location	Amount below 2 micron, percent
Point Arguello (sea spray)	10
Harbor Freeway (motor vehicle).	66
Goldstone (desert)............	50

An extrapolation method is required for the analogous interpretation of Brock's MMD data, except where MMD equals two micron. (For this exception, the fraction less than two micron is obviously 0.50). Brock (his page 15) implies that the particle size distribution, for comminution processes at least, can be approximated by a log-normal relationship. He doesn't specify a slope, and it would be unlikely that one slope would characterize all emission distributions. Nevertheless, I applied a single log-normal extrapolation to Brock's emission data such that:

Particle size MMD, micron	Amount below two micron, percent
10	6
2	50
0.2	99*

* Some feeling as to the reality of the extrapolation method can be obtained by comparing some extrapolated fractions with the distributions reported by hidy and Mueller (see my page 19).

For Point Arguello sea spray, the extrapolation method (based upon an area-derived seven micron MMD) yields 11 percent fine, while direct area measurement yields 10 percent fine.

For transportation, the direct area measurement of the Harbor Freeway size distribution yields 66 percent fine, while the weighted average of Brock's three transportation categories as extrapolated yields 38 percent (Exhibit 3). Even less satisfying, direct application of the extrapolation method to the Harbor Freeway distribution (using an area-derived 0.4 micron MMD) yields 94 percent less than two micron. The very irregular shape of the curve, caused by a mixture of sources, apparently causes the extrapolation method to yield the erroneous results.

The Goldstone desert comparison can not be used, since the area-derived two micron MMD must and does agree with the area-derived 50 percent below-two-micron fraction.

(End of footnote)

Results of the extrapolations are summarized on Exhibit 3. Addition of a 24th category, "miscellaneous, forest and agricultural fires", expands the Brock listing into an emission inventory which closely resembles that published by EPA and CEQ for 1969 or 1970 (Babcock and Nagda, 1972). This additional category, with an assumed one-micron MMD, is included on Exhibit 3. The revised inventory totals indicate that the fine fraction comprises 53 percent of the primary-PM emission total. Thus, at a given ambient location, the primary fine fraction could comprise a substantial part of the TSP total. For example, one could postulate a total particulate level of 100 μgram/meter^3 with 60 μgram/meter^3 in the fine and 40 μgram/meter^3 in the large fractions. The fine fraction could be made up almost exclusively of primary material, with only 7 percent secondary material needed to obtain closure (60 - 53 = 7).

The percentages below and above two micron are needed to allocate source emissions into size categories. These allocations can be derived directly as weighted averages using data on Exhibit 3, or by combining the percentages from Exhibit 3 with other summaries of source data (such as on Exhibit 4).

One result may be of interest here. The data on Exhibit 3 indicate that nationwide, fine primary emissions derived from stationary point sources comprise 25 percent of all the primary emissions listed on Exhibit 3 (8.91/35.20 = 0.25).

California composite characterization. Each of the input consultants referred to the work of Friedlander and co-workers, in which ambient PM was allocated amongst various source and species categories. Several related papers have been published describing and applying this characterization method. Gartrell and Friedlander (1975) has been utilized herein because it describes the most recent and comprehensive application of the methodology.

One of the significant features of their 1975 work is the attempt to obtain closure. Both measured and calculated TSP masses are presented for each of the five cities studied.

The following procedure was used to convert the Gartrell and Friedlander results (their Table 4) into Exhibit 6:

a. The Pasadena and Pomona data were complete (no unknowns) and, thus, the species and sources constituents were easily converted into percentages of the calculated total masses.
b. For Riverside, Fresno, and San Jose; organics and/or water were listed as unknowns. These unknowns were assumed equal to the same percentages as for the known categories for Pasadena and Pomona.
c. After estimation of the unknowns, the percentages of source and species constituents were determined for Riverside, Fresno, and San Jose.
d. The percentage results for each city were averaged together to arrive at a single California composite (Exhibit 4a).
e. Categories were rearranged to simplify reporting and to emphasize the point sources of interest to CSL: "industry and agriculture" was first disaggregated, with argiculture assumed to be 40 percent of the total (from San Francisco, Riverside and Fresno data reported by Gartrell and Friedlander, their Table 2); agriculture, sea salt, and soil dust were combined into a single so-called "natural" category; transportation sources, including auto exhaust, diesel exhaust, tire dust, and aircraft, were combined; cement dust was added to the industry category (although some cement dust might be generated from erosion, construction and demolition of concrete structures).

f. Distribution of the chemical species proved more difficult and subjective: of the 6 percent SO_4, 0.5 percent was allocated to the natural category and 5.5 percent to combustion; the 9.7 percent NO_3, was distributed equally between transportation and combustion.

The allocation of NH_4 is extremely subjective, but at the same time, quite essential to meaningful source assessment. Various ammonium salts have been defined as major constituents of secondary acid sulfates. Yet few investigators have even attempted to relate the ammonium back to sources, beyond the relatively large natural emissions which are known to exist. Photochemical reactions might create ammonia from precursors emanating from other kinds of sources. Thus, of the 4.5 percent NH_4, 1.5 percent was allocated to the natural category and one percent each to transportation, industry, and combustion.

Organics pose similar difficulties, since only rarely are individual species defined, and measurement involving benzene or other solvent extractions may not adequately describe the total organic content. Adding to the confusion, organics emanate from a diversity of natural and anthropogenic sources and are participants in a variety of ill-defined photochemical reactions. Lodge makes the point that emission inventories and other source assessments have tended to underestimate the significance of hydrocarbons and other organics which are derived from natural sources. Thus, the 23.7 percent for organics was distributed with four percent to industry and the remainder split equally between the natural and transportation categories.

Water was included in the characterization because it seems to comprise a significant percentage of the TSP total mass. However, no attempt was made at source allocation, since water usually isn't considered to be a pollutant, and there seems to be no meaningful way to differentiate between natural and emitted water.

The aggregrated source categories, with species allocated are summarized on Exhibit 4b.

g. At this point, it seemed illuminating to compare this distribution (Exhibit 4b) based upon data of Gartrell and Friedlander, with the nationwide emission distribution (Babcock and Nagda, 1972), with all pollutants summed except carbon monoxide. (Carbon monoxide was assumed not to cintribute to primary or secondary particulate matter.). The results, with water factored in, are also shown on Exhibit 4b. There appear to be two notable discrepancies between the two distributions. First, the natural-and-miscellaneous category is much larger when based upon California ambient measurements. This outcome seems reasonable, since several natural and fugitive sources are not included in the nationwide "miscellaneous" emission category; also, the low humidity common in California should cause relatively high levels of reentrained dust. The second discrepancy involves stationary combustion, with the California result being only 60 percent of that based on nationwide emissions. Two explanations come to mind. California does not use much coal as a fuel, and not all the emitted sulfur oxides and nitrogen oxides are transformed into particulate matter. No doubt both explanations have some validity.

In any event, the exercise of comparing California ambient results with nationwide emission averages, should instill some caution into those tempted to extend California results to other regions in the nation.

h. The next task was to distribute the species between the fine-size and large-size categories. Here, the previous assumptions as to species, results from Hidy and Mueller (my page 19), and the extrapolated data of Brock (Exhibit 3) were employed. Perhaps the most subjective allocation was for organics. The large number of sources and species and primary-secondary uncertainty seemed to preclude a meaningful distribution, so a 50-50 fine-large distribution was assumed.

i. Next, the distinction between primary and secondary was made. Again, previous assumptions with regard to SO_4, NO_3, NH_4, and organics were utilized.

j. The results, derived as indicated above, are summarized in tabular form on Exhibit 5a and were used to create Exhibit 6, the characterization diagram.

Nationwide characterization. A few attempts have been made to apply the methodology used by Gartrell and Friedlander to other parts of the country. However, none of these, as well as others attempts at characterization, seem to have been as comprehensive as the California characterizations. Particularly needed are complete characterizations of those regions with heavy industry, more coal combustion, and with meteorology less favorable to photochemical reactions. Much of the nation's urban population is exposed to such conditions, rather than to the relatively unusual California situations studied by Gartrell and Friedlander.

Rather than extrapolate from one of the less-comprehensive studies of a non-California region, it was decided to extrapolate the California data itself--to-more-closely approximate the emission conditions prevalent outside California.

The California composite was extrapolated into a nationwide characterization by applying the following conditions, solving algebraically, and then normalizing to 100 percent:

a. $SO_4/NO_3 = 1.4$ (from nationwide emissions inventory: $SO_2/NO_x = 1.4$, Babcock and Nagda, 1972).

b. Water = 12 percent (from California composite, Exhibit 5a).

c. $\frac{\text{Fine PM from industry and stationary combustion}}{\text{Total PM}} = 0.25$
(from Exhibit 3 as discussed on my page 21).

d. $\frac{\text{Industry fine PM}}{\text{Stationary combustion fine PM}} = 1.7$
(from Exhibit 3).

e. Fine PM = large PM, for primary stationary combustion (from Exhibit 3).

f. $\frac{\text{Industry inorganic large PM}}{\text{Industry organic large PM}} = 2.5$

(from California composite, Exhibit 5a).

g. $\frac{\text{Industry total PM}}{\text{Stationary combustion total PM}} = 2$

(from nationwide inventory, Babcock and Nagda, 1972).

The unnormalized results of the algebraic exercise are shown on Exhibit 5b, where the seven calculated quantities (algebraic unknowns) are shown in parentheses. The other quantities are duplicates of those for the California composite (Exhibit 5a). Note that the calculated nationwide TSP level is 59 percent greater than for the California composite. To enable comparison of the distributions, the results were normalized to 100 percent and are shown on Exhibit 5c.

Several interesting contrasts are apparent. In the nationwide inventory, primary fine PM and sulfates, are the cause of significant increases (above California) in the industry and stationary combustion categories. Although the absolute amounts in the natural and transportation categories remain unchanges, the relative contributions are reduced significantly in the normalized nationwide comparison.

The ratio of primary fine PM/large PM increases from 27 percent in the California composite to 50 percent for the nationwide characterization. The calculated 50 percent approaches the 53 percent result derived exclusively from Exhibit 3.

Additional discussion of the results is presented in the following section.

Discussion

This section contains some odds and ends which didn't seem to fit anywhere else. Considerable expansion of this section might be desirable, but time constraints dictated otherwise.

Residence time. Brock (his Table 9), based in part upon the work of Esmen and Corn emphasized the effect of particle size on atmospheric residence time:

Diameter (Microns)	Residence time (hours)
0.1	1622
0.5	324 (assumed MMD for fine PM)
1	162
10	14 (assumed MMD for large PM)
15	10
20	7
40	4
100	1.4

A large variation is apparent, but note that even the 100 micron particles would be expected to stay airborne for a distance of 14 miles in a 10 mile/hour wind. Thus, it seems reasonable to assume that all-sized particles stay airborne, at least within the immediate urban region. This conclusion seems to support some of the assumptions leading toward the characterization diagrams. However, Brock's opposite conclusion also seems well justfied when applied to the nationwide airshed. The small particles are the ones which increasingly comprise the bulk of the aerosol, as distances from large sources increases.

Limits. On a nationwide basis, it seems to be possible to use the extrapolated Brock data to define "floating" limits for the maximum percentages of primary fine particulates from the various categories. For example, if there were no secondary particulates, and if all particles remained airborne for the same length of time, Exhibit 3 could be used to define the TSP problem. Calculations based on Exhibit 3 indicate:

	Percentage of primary emissions below two micron	
Natural and miscellaneous	24	
Transportation	4	
Stationary combustion	13	25%
Industrial	12	
Total below two micron:	53	

This tabulation indicates that 25 percent of the ambient fine PM in TSP could be derived from anthropogenic stationary sources if there were no contribution from secondary PM pollutants. Any presence of secondary pollutants would decrease the percentage of primary fine PM emissions from anthropogenic stationary sources. Conversely, at greater distances from sources, fall out of the large particles as discussed above, could increase the percentage of primary anthropogenic fine PM.

Extrapolation of Friedlander results. My extension of Friedlander results to a nationwide characterization is certainly open to criticism. It might now be useful to compare some of the existing non-California studies with the nationwide characterization described in this report. Of course, most needed are comprehensive experimental characterizations of several types of non-California cities. Also, more thought as well as experiments are warranted with regard to how best to expand the Friedlander approach to a total source-species-size characterization. In fact, Prof. Friedlander, himself, might choose to extrapolate his results in a manner such as to arrive at conclusions quite different from those presented herein.

Definition of particle-size distribution. There seems to be sufficient experimental data to justify the conclusion that ambient particle size distributions tend to be bimodal on a mass or volume basis. There is less agreement as to where the minimum occurs. Two mocrons was selected for use in this report and represents a sort of maximum size for this minimum point in the distribution.

There seems to be least justification for assuming that the entire fine PM fraction consists of secondary PM. There must be primary emissions of fine PM, and in this report, I have tried to extend Brock's data to define the amounts emitted from different source categories. Combustion sources appear to be the largest source of the primary fine PM (probably as uncombined carbon).

While examining the relative significance of primary fine PM, the question arose as to the hypothetical shape of an ambient distribution, if there were no transformations, and all ambient PM were derived from primary emissions. The ambient distribution still could be bimodal if there were sufficient fine (or sub-fine) PM generated. (See Exhibit 2, curve 3). Such primary fine material would be expected to coagulate in the same manner as secondary material, until constrained by the termination of Brownian motion mechanism at the larger particle sizes (one to two micron). Such reasoning might partially explain the bimodal distribution reported by Hidy and Mueller for the relatively non-anthropogenic Goldstone location.

Primary versus secondary. Much of recent literature has stressed the presence of the secondary constituent of TSP. The emphasis has led some to assume that the secondary constituent is usually dominant in ambient air, and the question is confused if one also assumes that secondary and fine PM are synonymous. This report identifies a sizable primary-fine constituent which reduces the fraction of fine PM which can be allocated to secondary constituents. Further, the input reports all present information describing situations where primary and/or large PM was found to be dominant.

The characterization results, as summarized on Exhibit 8, can also be directed to the question. The percentages of secondary are 32 and 25 percent for the California composite and nationwide, respectively. Both are significant fractions of the total, but neither is dominant. Also note that the total fine fraction is larger for the nationwide characterization, but the increase is due to the primary fine fraction rather than to secondary pollutants.

At this point, the reader might review Exhibit 2. The California composite (curve 1 on Exhibit 2) and nationwide characterizations (curve 2 on Exhibit 2) seem to have roughly equal fractions in each size category (as shown on Exhibit 2), but the composition within the fine mode may be quite different. Further resolution awaits more rigorous characterization of the fine mode. Quantification of the combustion carbon fraction would be particularly enlightening.

Impact of water and natural species. The results, summarized on Exhibit 8, indicate a sizable contribution (36-51 percent) from water and so-called "natural" sources. (Recall that the "natural" category includes fugitive dusts and emissions from forest and agricultural fires.) Information in the input reports and elsewhere indicates that these categories often comprise highly significant fractions in ambient aerosols. Policy makers should be more aware of their presence, since these categories appear to pose quite a constraint in meeting ambient air quality standards.

Note how Exhibit 8 would change if these "natural" sources were removed. For example, in the nationwide characterization, primary fine PM from stationary sources would increase from 16 to 25 percent.

Definition of TSP. Much of the difficulty in defining 100 percent of the constituents of TSP lies in our inability to accurately measure the total mass of TSP itself. Presently, we rely almost exclusively on the high vol, but two of the input consultants mentioned the problems associates with reactions taking place upon the mat (mass is increased) and with volatile particulate matter evaporating from the map (mass is decreased). Water was included in the presented characterizations, in part to bring attention to the problem of quantification of volatile particulate matter.

Rather than TSP (total suspended particulates), it has been suggested that PM might be better defined as TFP (total filterable particulates). Considerable research on these basic mass measurement methods seems desirable. The discrepancy between some cascade-type samplers (for particle size distribution) and the high vol (for total particulate mass) is particularly disturbing.

One must question not only the characterizations but the epidemiological studies derived from the characterizations. (Lodge makes the point well on his pages 2-3.)

Emission monitoring. Concern with regard to measurement adequacy should also extend to emission monitoring. Many assumptions were required herein because of the lack of adequate emission characterization. Unfortunately, controlversy shrouds even the definition of what is a particle, not to mention the much needed emission size distributions. Of particular interest would be better definition of that PM which is formed almost at the stack exit. Should such PM be considered primary, secondary, or is a third category needed?

Relative toxicity. This report emphasizes the relative masses associated with various sources, sizes and species. It should be noted that it is unlikely that all the species and sizes have the same toxicity. Yet such is at least tacitly assumed when making mass comparisons. It seems likely that incorporation of pindex-type toxicity-based weighting factors (Babcock and Nagda, 1972) might increase the significance of some of the primary stationary source PM (trace metals, asbestos, specific-organics), at least over that of some of the natural and secondary pollutants. The reader should consider such possibilities, but because of data limitations, quantitative treatment presently seems unattainable.

Conclusions

It seems clear that there is no single generalized source-species-size characterization which is applicable throughout the nation. The various distributions may all tend toward bimodal, but the sources and species appear to vary significantly from location to location, depending on local sources. Adding further complexity, the relationship between source and ambient air quality seems to vary significantly from season to season and even hour to hour. The incomplete distributions published to date are probably not representative of their own regions, much less of the nation as a whole. The uncertain results presented herein are summarized on Exhibit 8 and might best be interpreted as ranges, that most of the nation's characterizations would lie somewhere in between the California and nationwide results.

Both characterizations indicate significant contributions from water and from natural-and-miscellaneous sources. These findings support the contentions of Lodge and define a significant problem to control officials. Much more effort should be directed toward these sources (other than water) which are largely uncontrolled at present.

Transportation remains a significant problem in both characterizations, but it is not the dominant category, even in California.

Finally, even when transformations and secondary pollutants are considered, stationary combustion and industrial sources remain the major anthropogenic sources of TSP (26-49 percent of TSP total). These same stationary combustion and industrial sources contribute a not-dominant, but still-significant fraction of TSP in the form of fine primary PM emissions (4-16 percent of the TSP total). Continued research directed toward control of these fine-size emissions seem well justified.

Postscript

This report has attempted to integrate some existing information in an effort to better relate emissions with ambient PM characterization and levels. By inferences, the report should also serve to help define the considerable gaps in our present knowledge.

The two characterizations presented on Exhibits 6 and 7 certainly contain a large number of questionable assumptions, but these results do seem to be logically derived from information contained in the input reports. Perhaps I succumbed to over use or over interpretation of the meager data available, but it seems that pursuit of this temptation was a fundamental purpose of the study--to draw conclusions based upon available information. Hopefully, these conclusions will serve to generate discussion and further study, as well as generation of more complete experimental characterizations.

Two deficient areas are readily apparent. First, much increased effort should be directed toward size-specific and species-specific emission inventories. It should be unnecessary to have to exclusively work backwards from ambient data. Better characterization of primary emissions would multiply the utility of comprehensive characterization of ambient air environments. Characterizations should be conducted on a size basis, not only in California, but in other regions.

As new information becomes available, the characterizations presented on Exhibits 6 and 7 may warrant significant revisions. I hope my pleas will be heeded, that future characterizations will be reported as percentages of TSP total, even if an unknown category must be included. Characterizations published as percentage of known, of secondary, of fine PM, etc., tend to be confusing, if not misleading. The characterization diagram is proposed as a straightforward means for presenting results on a TSP basis.

Some readers may already be eager to draw conclusions contrary to those presented herein. Toward this end, a blank characterization diagram is enclosed (Exhibit 9). Generation, comparison, and evaluation of alternative conclusions in itself seems a worthwhile outcome of this study.

Acknowledgment

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Exhibit 3. Primary Emission Distribution

	Mass Median Diameter,[a] Micron	Below Two Micron, Percent	Emissions, 10^6 ton/year	
			Total[a]	Below Two Micron
Coalfired elec utility	2.0	50	3.36	1.68
Ind power	2.0	50	3.22	1.61
Crushed stone	10.0	6	5.71	0.34
Agric opn	10.0	6	1.84	0.11
Iron & Steel	0.4	94	1.31	1.23
Cement	3.0	36	0.96	0.35
Pulpmills	1.0	76	0.56	0.43
Time	2.0	50	0.65	0.32
Non-ferrous metals	1.0	76	0.73	0.55
Clay	3.0	36	0.54	0.19
Fertilizers	1.0	76	0.30	0.23
Phosphate rock	2.0	50	0.06	0.03
Asphalt	1.0	76	0.22	0.17
Ferro alloys	0.4	94	0.16	0.15
Iron foundaries	0.4	94	0.15	0.14
Coal cleaning	2.0	50	0.11	0.06
Petroleum	0.5	92	0.05	0.05
Acids	0.4	94	0.02	0.02
Solid waste disposal	0.3	97	1.40	1.36
Construction dust	5.0	18	0.80	0.14
Transportation combustion	0.4	94	1.20	1.13
Transportation tire dust	3.0	36	0.30	0.11
Transportation road dust	5.0	18	1.00	0.30
Miscellaneous forest & Agricultural fires	1.0	76	10.55	8.02
TOTAL			35.20	18.72

[a] from Brock, Table 9

Exhibit 4. Preliminary Characterizations

Exhibit 4a California composite (before distribution of secondary species)

Category	Mass, percent
Sea salt	3.0
Soil dust	19.5
Auto exhaust	3.7
Cement dust	1.6
Fly ash	0.1
Diesil exhausts	1.0
Tire dust	0.4
Indust. and Agric.	12.3
Aircraft	2.2
SO_4	6.0
NO_3	9.7
NH_4	4.5
Organics	23.7
Water	12.3
Total mass	100.0

Exhibit 4b Aggregated California composite and nationwide inventory

Category	California Composite[a]	Nationwide Inventory[b]
Natural and Miscellaneous	35	14
Transportation	19	23
Industry[c]	16	22
Stationary combustion	18	29
Water	12	12
	100	100

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a - derived from Exhibit 4 a

b - from Babcock and Nagda: summation of all pollutants except carbon monoxide; normalized to include 12 percent water

c - includes solid waste

Exhibit 5. Detailed characterizations

		Above two micron		Below two micron						
		Primary			Secondary					
		Inorganic incl SO_4 & Carbon	Organic	Other inorganic & Carbon	Organic	NH_4	NO_3	SO_4	Water	Total
5a:	California composite									
	Natural & miscellaneous	26	5	2	5	1				39
	Transportation	1	5	6	5	1	5			23
	Industry	5	2	4	2	1				14
	Stationary combustion	0	0		0	1	5	6		12
	Water								12	12
	TOTAL	32	12	12	12	4	10	6	12	100
5b:	Nationwide (unnormalized: California composite=100%)									
	Natural & miscellaneous	26	5	2	5	1				39
	Transportation	1	5	6	5	1	5			23
	Industry	(15)	(6)	(16)	2	1				40
	Stationary combustion	(9)	0	(9)	0	1	5	(14)		38
	Water								(19)	19
	TOTAL	51	16	33	12	4	10	14	19	159
5c:	Nationwide (normalized)									
	Natural & miscellaneous	16	3	1	3	1				24
	Transportation	1	3	4	3	1	3			15
	Industry	9	4	10	1	1				25
	Stationary combustion	6		6	0	1	3	8		24
	Water								12	12
	TOTAL	32	10	21	7	4	6	8	12	100

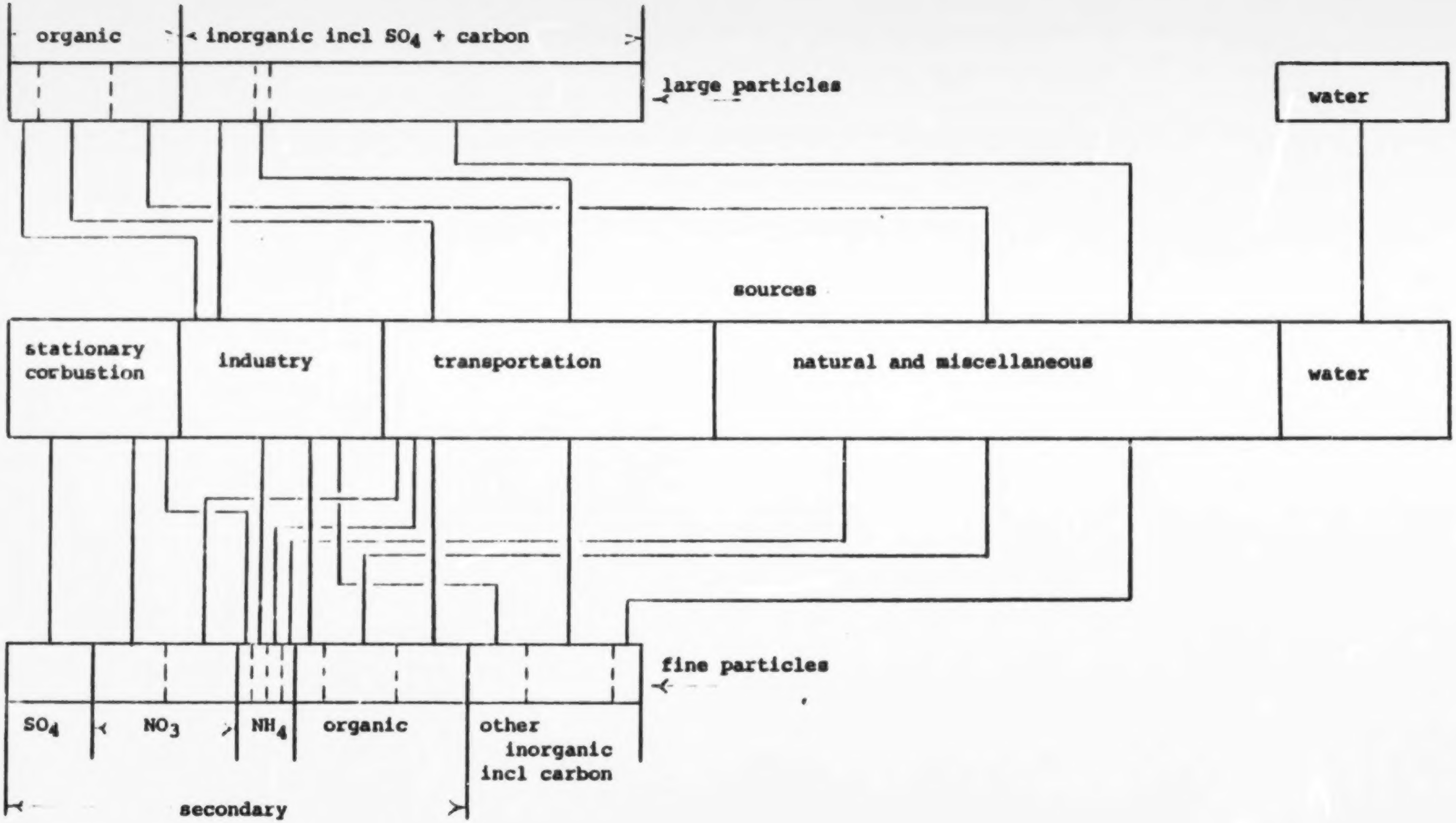

organic
inorganic incl SO_4 + carbon
large particles
water
sources
stationary corbustion
industry
transportation
natural and miscellaneous
water
fine particles
SO_4
NO_3
NH_4
organic
other inorganic incl carbon
secondary

Exhibit 6. California composite characterization diagram

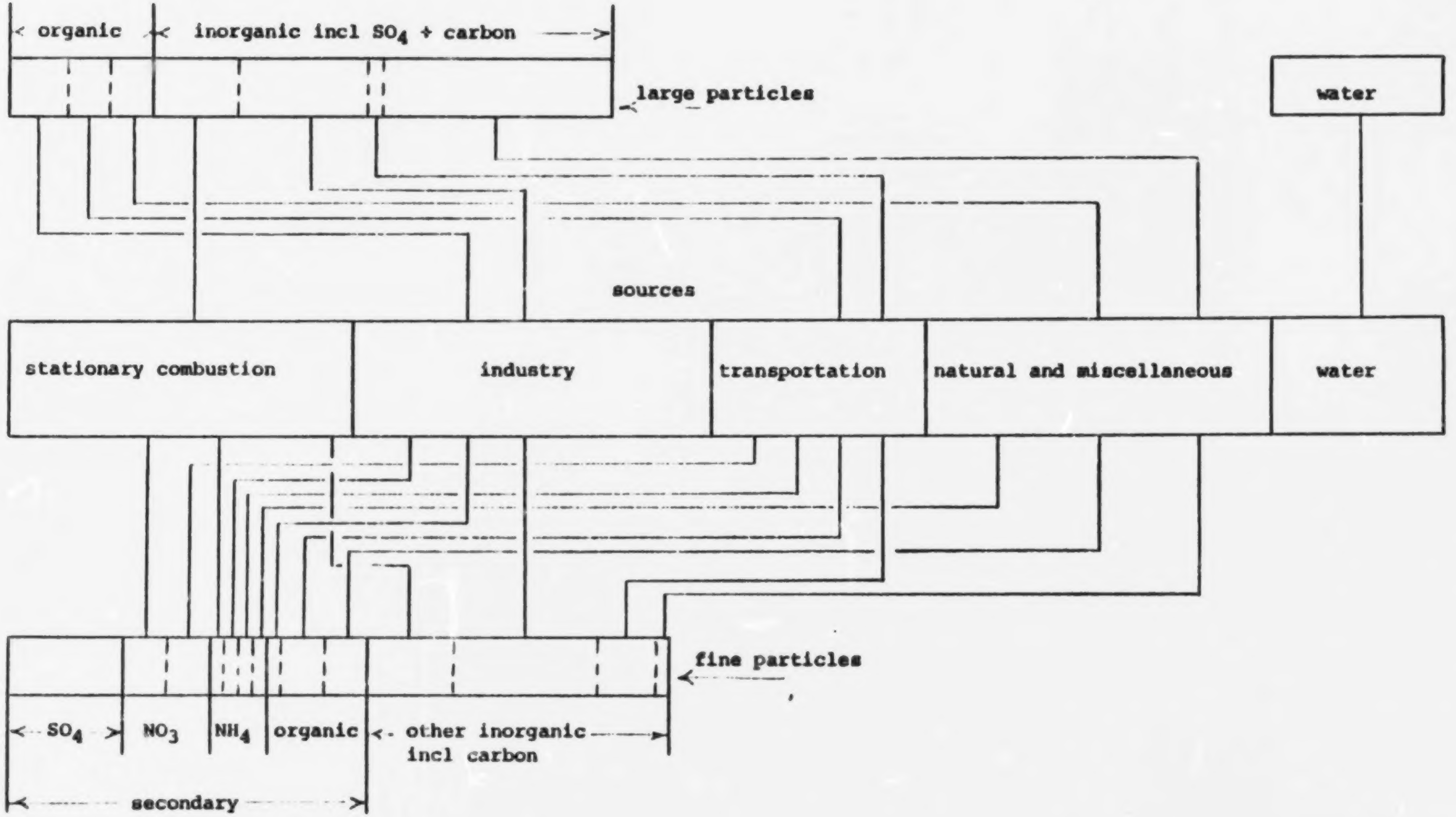
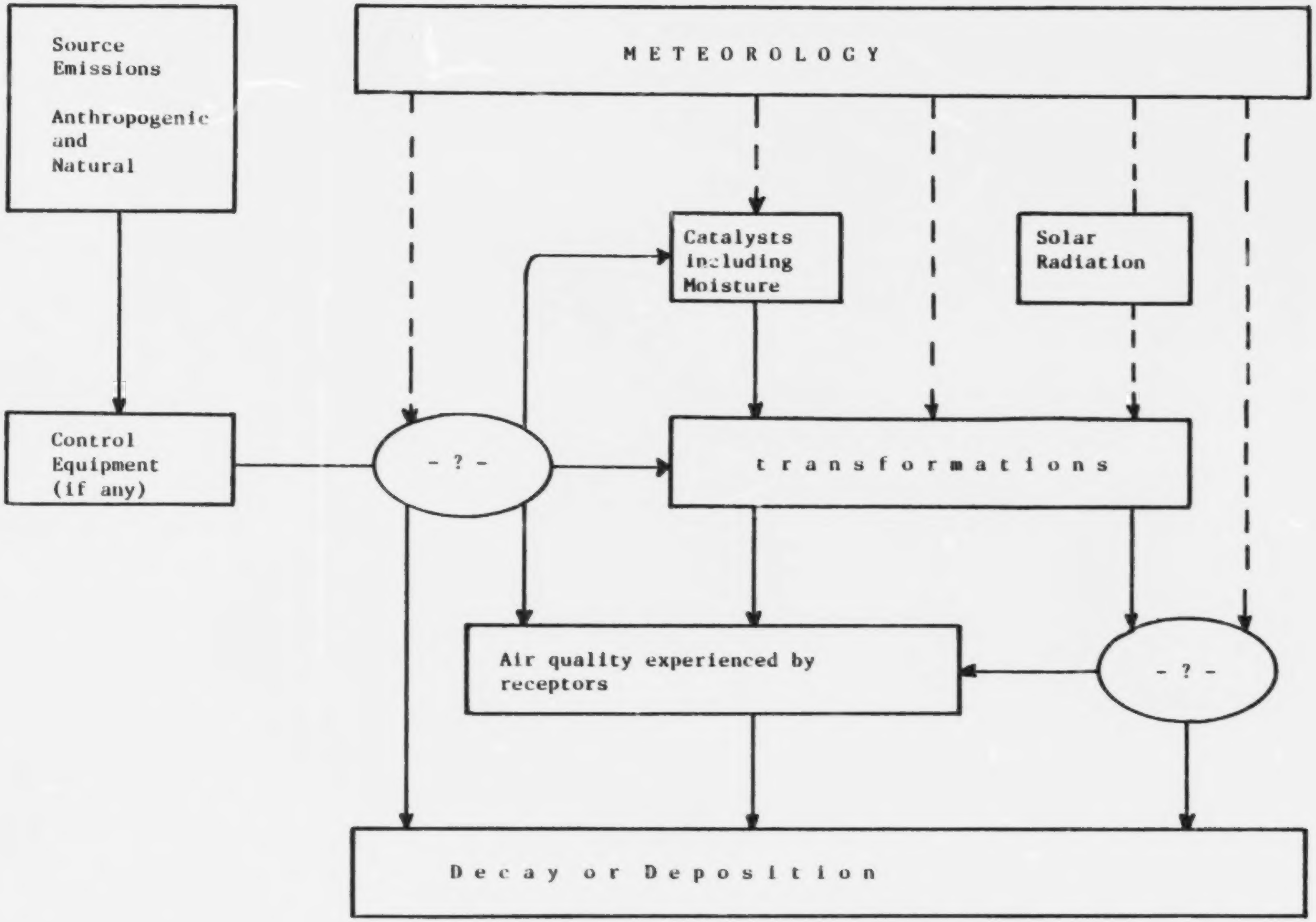

organic
inorganic incl SO_4 + carbon
large particles
water
sources
stationary combustion
industry
transportation
natural and miscellaneous
water
fine particles
SO_4
NO_3
NH_4
organic
other inorganic incl carbon
secondary

Exhibit 7. Nationwide characterization diagram

Exhibit 8. Summary Comparison

Category	California	Nationwide
Combustion and industry	26	49
Transportation	23	15
Natural and miscellaneous	39	24
Water	12	12
TOTAL	100	100
Secondary PM	32	25
Primary fine PM (from stationary sources)	4	16
Other Primary fine PM	8	5
Large PM	44	42
Water	12	12
TOTAL	100	100


Source Emissions
Anthropogenic and Natural
METEOROLOGY
Catalysts including Moisture
Solar Radiation
Control Equipment (if any)
- ? -
transformations
Air quality experienced by receptors
- ? -
Decay or Deposition

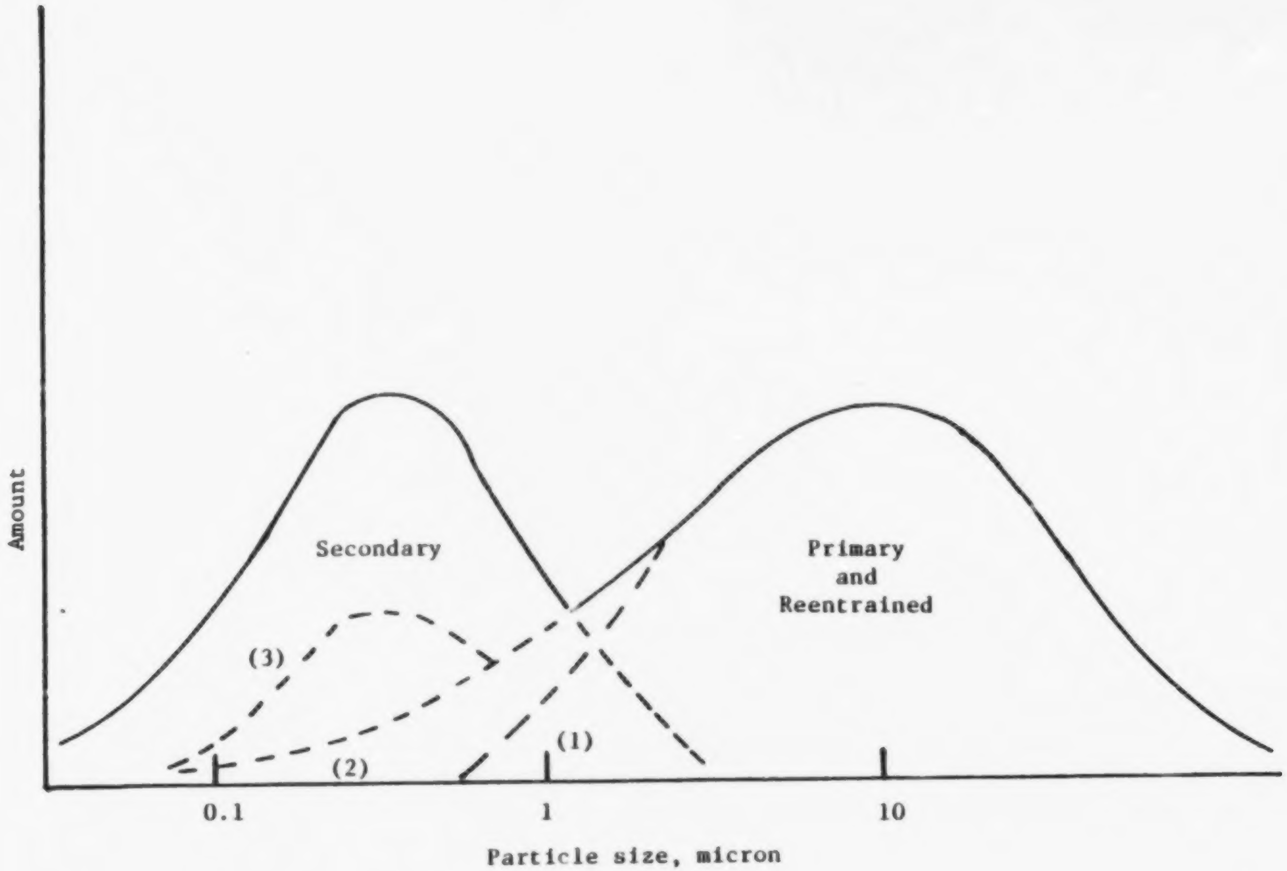


Exhibit 2. IDEALIZED PARTICLE-SIZE DISTRIBUTIONS